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CERTIFICATION REPORT

The Certification of the Mass Fraction of the Total Content and the Aqua Regia Extractable Content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in Loam Soil

Certified Reference Material ERM®-CC141

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European Commission
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Contact information
Reference materials sales
Retieseweg 111
B-2440 Geel, Belgium
E-mail: jrc-irmm-rm-sales@ec.europa.eu
Tel.: +32 (0)14 571 705
Fax: +32 (0)14 590 406

http://irmm.jrc.ec.europa.eu/
http://www.jrc.ec.europa.eu/

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The Certification of the Mass Fraction of the Total Content and the Aqua Regia Extractable Content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in Loam Soil

Certified Reference Material ERM®-CC141

A. Birgersson-Liebich, T. Venelinov, A. Santoro, A. Held

European Commission, Joint Research Centre
Institute for Reference Materials and Measurements (IRMM), Geel (BE)

Disclaimer

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Summary

This report describes the preparation and certification of the loam soil Certified Reference Material (CRM) ERM-CC141. The CRM was processed and certified by the European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

The CRM was prepared from a loamy soil with a natural level of metals. After being dried and milled, the resulting soil powder was put into amber glass bottles containing a minimum of 24 g of sample.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

The CRM has been certified for its total and its aqua regia extractable (according to ISO 11466) content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn.

The main purpose of the material is to assess method performance and check analytical results. As any reference material, it can also be used for control charts or validation studies.

Total content	Mass fraction based on dry mass	
	Certified value [1] [mg/kg]	Uncertainty [2] [mg/kg]
As	9.9	1.5
Cd	0.35	0.05
Co	8.5	0.5
Cr	86	8
Cu	14.4	1.4
Mn	464	18
Ni	26.4	2.4
Pb	41	4
Zn	57	4
Aqua regia extractable content according to ISO 11466	Mass fraction based on dry mass	
	Certified value [1] [mg/kg]	Uncertainty [2] [mg/kg]
As	7.5	1.4
Cd	0.25	0.04
Co	7.9	0.9
Cr	31	4
Cu	12.4	0.9
Mn	387	17
Ni	21.9	1.6
Pb	32.2	1.4
Zn	50	4

1) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values are traceable to the SI.

2) Expanded uncertainty with a coverage factor $k = 2$ according to the Guide for the Expression of Uncertainty in Measurement, corresponding to a level of confidence of about 95 %.

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Glossary

ANOVA	analysis of variance
BCR	Community Bureau of Reference
c	concentration
CI	confidence interval
CRM	certified reference material
ED-XRF	energy dispersive X-ray fluorescence spectrometry
ET-AAS	electrothermal atomic absorption spectrometry
HR-ICP-MS	high resolution inductively coupled plasma - mass spectrometry
ICP-MS	inductively coupled plasma – mass spectrometry
ICP-SFMS	inductively coupled plasma – sector field mass spectrometry
ID-ICP-MS	isotope dilution - inductively coupled plasma – mass spectrometry
ICP-OES	inductively coupled plasma – optical emission spectrometry
ISO	International Organization for Standardization
k	coverage factor
k_0-NAA	neutron activation analysis using the k_0-method for quantification
$MS_{between}$	mean square between bottles from an ANOVA
MS_{within}	mean square within a bottle from an ANOVA
n	average number of replicates per bottle
RSD	relative standard deviation
s_{bb}	between bottles standard deviation
s_{wb}	within bottles standard deviation
SD	standard deviation
SI	Système International d'Unités (International System of Units)
t	proposed shelf-life
$\bar{t}$	average of all time points
t_i	time point for each replicate
TC	total carbon
TIC	total inorganic carbon
TOC	total organic carbon
u_{bb}	uncertainty related to a possible between bottles inhomogeneity
u_{bb^*}	uncertainty of inhomogeneity that could be hidden by method repeatability
u_c	combined standard uncertainty of the certified value
u_{char}	uncertainty of the characterisation
u_{CRM}	standard uncertainty of a certified value
U_{CRM}	expanded uncertainty of a certified value
u_{lts}	uncertainty of long-term stability
u_{meas}	standard measurement uncertainty
u_R	relative uncertainty due to repeatability
u_{st}	relative uncertainty of the calibration standard
$v_{MSwithin}$	degrees of freedom of MS_{within}
XRF	X-ray fluorescence spectrometry
$\bar{y}$	average of all results of a homogeneity study

1 Introduction

The Certified Reference Material ERM-CC141 described in this report is intended to replace BCR-141R Calcareous Loam Soil of which the present supply has expired. BCR-141R Calcareous Loam Soil was part of a set of three soil reference materials including BCR-142R Light Sandy Soil and BCR-143R Sewage Sludge Amended Soil. These materials, which together covered different concentrations of trace elements and different matrices, were mainly intended for the verification of accuracy of trace element determinations in soils or other similar matrices.

In order to plan the ERM-CC141 production, care was taken to find a material with a composition close to that of the original soil BCR-141R. However, it has to be taken into account that the selection of these two materials was separated by a period of 10 years and a distance of more than one thousand kilometres. Therefore in the present material a difference in the content of some trace elements and of some major components occurs.

As the information on the aqua regia soluble content of some elements was a very useful tool for the users of the previous CRM (BCR-141R), certification of this quantity was also decided upon.

2 List of participants

Project management

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel (BE) – *ISO Guide 34 accreditation*

Sampling and Processing

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol (BE)

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel (BE)

Microhomogeneity Study

ALS Laboratory Group, ALS Scandinavia AB, Luleå (SE) - *Measurements performed under ISO/IEC 17025 accreditation; SWEDAC-1087*

Homogeneity Study

Energy Research Centre of the Netherlands (ECN), Petten (NL)

Stability Study

Minton Treharne & Davies Ltd (MTD), Herbert J Evans Division, Carmarthenshire (UK) - *Measurements performed under ISO/IEC 17025 accreditation; UKAS, 0024*

The Macaulay Institute, Analytical Service, Aberdeen (UK) - *Measurements performed under ISO/IEC 17025 accreditation; UKAS, 1917*

Characterisation Measurements

ALS Laboratory Group, ALS Czech Republic, Prague (CZ) - *Measurements performed under ISO/IEC 17025 accreditation; CAI, 521*

ALS Laboratory Group, ALS Scandinavia AB, Luleå (SE) - *Measurements performed under ISO/IEC 17025 accreditation; SWEDAC-1087*

Centre National de la Recherche Scientifique (CNRS), Service Central d'Analyse, Solaize (FR)

Energy Research Centre of the Netherlands (ECN), Petten (NL)

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel (BE) - *Measurements performed under ISO/IEC 17025 accreditation; BELAC, 268-TEST*

Helmholtz Zentrum München, Deutsches Forschungszentrum für Gesundheit und Umwelt (GmbH), München (DE) - *Measurements performed under ISO/IEC 17025 accreditation; DACH, DAC-PL-0141-01-10*

Laboratory of the Government Chemist (LGC), Teddington (UK) - *Measurements performed under ISO/IEC 17025 accreditation; UKAS, 0003*

Minton Treharne & Davies Ltd (MTD), Herbert J Evans Division, Carmarthenshire (UK) - *Measurements performed under ISO/IEC 17025 accreditation; UKAS, 0024*

Studiecentrum voor Kernenergie, SCK, Mol (BE) - *Measurements performed under ISO/IEC 17025 accreditation; BELAC, 015-TEST*

The Macaulay Institute, Analytical Service, Aberdeen (UK) - *Measurements performed under ISO/IEC 17025 accreditation; UKAS, 1917*

Umweltbundesamt GmbH, Prüfstelle für Umwelt-, GVO- & Treibstoff-Analytik, Wien (AT) - *Measurements performed under ISO/IEC 17025 accreditation; BMWA-92.714/0518-I*

Universidad de Santiago, Facultad de Quimica, Departamento de Química Analítica, Santiago de Compostela (ES)

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol (BE) - *Measurements performed under ISO/IEC 17025 accreditation; BELAC, 045-TEST*

3 Processing

The loam soil used for the production of ERM-CC141 was collected in Dilbeek near Brussels (Belgium), from an undisturbed grass field. During the sampling, the upper soil layer including the grass and root zone was removed in an area of ca. 1m x 1m. Approximately 300 kg soil was sampled over this area. Stones, plant litter and wood pieces were removed manually. The soil was classified as loamy according to the Belgian Soil Database [9].

The material was dried in a drying cabinet UT6760 (Heraeus, Langenselbold, Germany) at + 29 °C until a target water content of 3-4 % was reached (21 days). After the drying was completed, a mass loss from 11.1% to 14.0 % (m/m) was found. The material was processed through a Retsch (Haan, Germany) jaw crusher and then subjected to a sieving step with a 1 mm sieve. The coarser part was crushed and sieved again; in this way, a total of 113 kg of dry soil was obtained. Further processing in a jet mill 100 AGF (Alpine, Augsburg, Germany) resulted in 110 kg of final material with a maximum particle size of 100 µm (average particle size ca. 30 µm). The particle size distribution of the material was assessed using a Helos laser light scattering instrument (Sympatec, Germany). As supplementary information, a typical particle size distribution and a micrograph of the ERM-CC141 are shown in Figure 1, and Figure 2, respectively.

Homogenisation was done for 5 hours in a cone mixer. A minimum of 24 g of the soil was filled in 100 mL amber glass bottles. A total of 4183 bottles was finally produced.

The filled bottles were sent to Nederland (Isotron Nederland B.V.) for gamma irradiation. The minimum irradiation dose used to sterilise the soil in the bottles was 10.0 kGy.

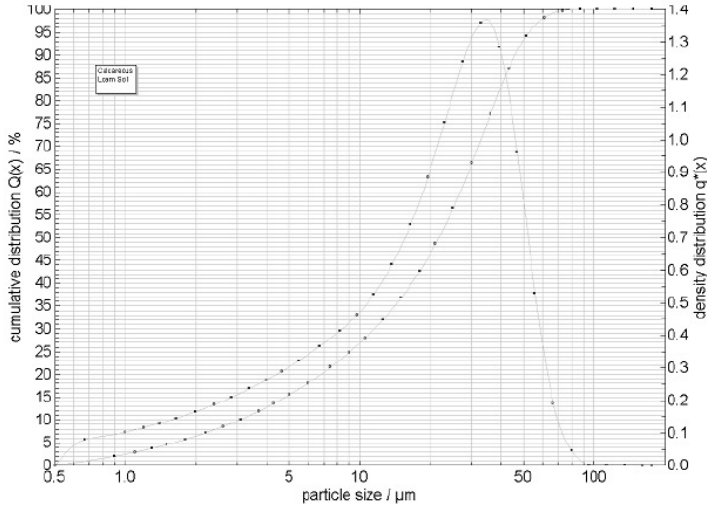

Figure 1: Typical particle size distribution for ERM-CC141

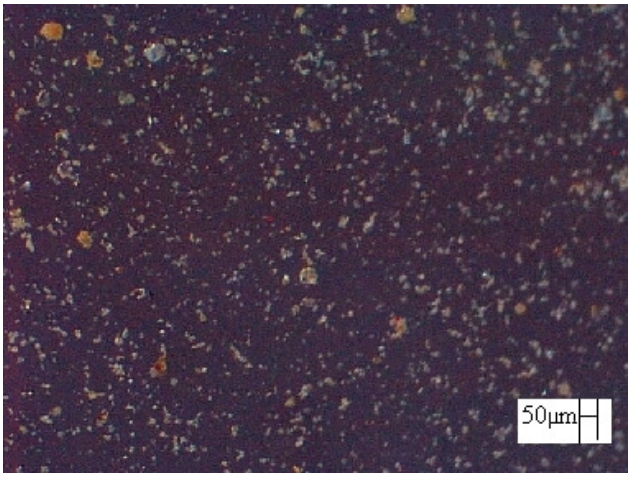

Figure 2: Micrograph of ERM-CC141

4 Homogeneity

4.1 Minimum sample intake

The minimum sample intake defines the minimum amount of sample that is representative for the whole unit. Therefore, samples above the minimum sample intake guarantee the certified value, which on the other hand is not true for subsamples smaller than the minimum sample intake because of micro-homogeneity problems that may occur.

The sample intake for the determination of the aqua regia extractable content of the elements is given in ISO 11466 [1]. Therefore no minimum sample intake has to be determined for this method.

The sample intake for the determination of the total element content was assessed combining the results of two approaches. The first one (A) consisted of analysing decreasing sample intakes until the results showed that the sampling of the material contributes significantly to the uncertainty of the analytical results. Sample intakes of 200 mg, 100 mg and 50 mg were analysed by using ICP-SFMS (Annex 1, Table A1). Three replicates of two bottles, for a total of six measurements for every element were performed. The final data were evaluated using single-factor ANOVA. Standard deviations within bottles (s_{wb}) and between bottles (s_{bb}) were calculated. As the within bottles heterogeneity is closely correlated to the minimum sample intake, the sample intake with lowest s_{wb} was chosen. Where more than one sample intake was found to be suitable, the preferred one was chosen using $s_{wb} < 2 \times s_{bb}$ as selection criterion.

The second approach (B) considered the minimum sample intakes used by the laboratories in the characterisation study of the CRM. The smallest amount of sample that has been applied to obtain a technically valid set of results accepted for the characterisation of the material can be used as minimum sample intake (Annex 1, Table A3).

The resulting minimum sample masses are summarised in Table 1.

Table 1: Minimum sample masses for total element contents in ERM-CC141 determined by using the two different approaches A and B.

Analyte	Sample mass [mg] assessed by using approach A	Sample mass [mg] assessed by using approach B
As	50	200
Cd	50	100
Co	200	100
Cr	200	100
Cu	100	100
Mn	50	100
Ni	50	100
Pb	100	100
Zn	50	100

As result of the combined study, a minimum sample intake of 100 mg was set for all elements. The 200 mg sample intake found for Co and Cr in the dedicated study (approach A) as well as for As in approach B might have been due to limitations of the method repeatability (ICP-SFMS and ICP-MS respectively) and not to the inhomogeneity of the subsamples.

The sample intake for the determination of the aqua regia extractable content of the elements, as prescribed in ISO 11466, is 3.0 g [1].

4.2 Between bottles homogeneity

The between bottles homogeneity is tested to ensure that the certified values of the CRM are valid for all bottles of the material, within the stated uncertainty. This was carried out using a dedicated test for u_{bb} evaluation for the total content and by using the data of the short term stability study for the aqua regia extractable content u_{bb} evaluation (paragraph 5.1).

Sixteen bottles were selected throughout the produced batch for the dedicated study in a random stratified manner [2]; three replicates have been measured per bottle by using ICP-OES (see Annex 1, Table A2). The results of these measurements were evaluated using the approach described by Linsinger *et al*. [3].

The obtained data were first tested to determine whether they follow a normal, or at least unimodal distribution. This was done by visual inspection of normal probability plots and histograms. If the data do not follow at least a unimodal distribution, the calculation of standard deviations is doubtful or meaningless. The data were also tested for outliers using the single and double Grubbs test for individual values and bottle averages. Further, the data were tested for a trend in bottle averages, which would indicate a discrimination effect during bottling, and a trend in the analytical sequence.

The results of the measurements are shown in Annex 2, while the results of the descriptive evaluation are summarised in Table 2.

Table 2: Statistical test of the homogeneity data for total content, measured using ICP-OES

Analyte	Distribution of individual results		Distribution of bottle means		Outliers		Significant trends (95 % confidence)	
	Normal	Unimodal	Normal	Unimodal	Individual values	Bottle average	Analytical sequence	Filling sequence
As	yes	yes	approx.	yes	none	none	no	no
Cd	yes	yes	yes	yes	none	none	no	no
Co	yes	yes	yes	yes	none	none	yes	no
Cr	no	yes	yes	yes	one	none	no	no
Cu	yes	yes	approx.	yes	one	one	yes	no
Mn	yes	yes	approx.	yes	none	none	no	no
Ni	no	approx.	no	approx.	one	one	no	no
Pb	yes	yes	approx.	yes	none	two	yes	yes
Zn	yes	yes	approx.	yes	none	one	no	yes

As reported in Table 2, all the distributions follow at least a unimodal distribution. In particular, for As, Cd, Co and Mn, individual results and sample means show mainly a normal distribution not affected by outlying values. Outliers were detected by a Grubbs test in the dataset of individual values for Cr, Cu and Ni, being significant at 95 % and 99 % confidence level and were also found in the bottle average values for Cu and Ni at 95% and 99% confidence level and for Pb and Zn at 95 % confidence level. Since no technical reason for the outliers could be found, all data were retained for statistical analysis. However, due to this reason, individual results and sample means might not follow a normal distribution, but unimodal.

In the specific case of Ni, the outlying result was found to be nearly twice as high as the others. Including this result in the evaluation, results in a distribution of the individual results and bottle means only approximately unimodal. For this reason, the uncertainty contribution due to Ni inhomogeneity was modelled by a rectangular distribution.

The regression analysis showed that the mass fraction of Pb and Zn decreased with increasing bottle number. These trends in the filling sequence were significant on a 95 % confidence level, but not on a 99 % confidence level. However, this trend is not confirmed by the statistical evaluation for aqua regia extractable content (Table 3), bringing about the conclusion that it could be rather due to an analytical artefact than a real trend in the filling procedure. Trends in the analytical sequence were also visible for Co, Cu and Pb, pointing at instability of the analytical system. These were again only significant on a 95 %, but not on a 99 % confidence level and no drift correction was applied.

Regarding the aqua regia extractable content, the homogeneity was evaluated by using data from short-term stability study. The results for all the samples stored at 18 °C and at 60 °C (for a total of 21 samples) were used for the evaluation (Table 3).

Table 3: Statistical test of the short term stability data for aqua regia extractable content measured using ICP-OES for As, Co, Cr, Cu, Mn, Ni, Pb and Zn and ICP-MS for Cd

Analyte	Distribution of individual results		Distribution of bottle means		Outliers		Significant trends (95 % confidence)	
	Normal	Unimodal	Normal	Unimodal	Individual values	Bottle average	Analytical sequence	Filling sequence
As	yes	yes	yes	yes	none	none	no	no
Cd	no	yes	no	yes	one	none	no	no
Co	no	approx.	no	approx.	one	two	no	no
Cr	approx.	yes	approx.	yes	no	one	no	no
Cu	approx.	yes	approx.	yes	one	no	no	no
Mn	yes	yes	approx.	approx.	no	no	no	no
Ni	approx.	yes	approx.	yes	one	no	no	no
Pb	yes	yes	yes	approx.	no	no	no	no
Zn	no	yes	no	yes	one	one	no	no

In this case, individual results referring exclusively to the aqua regia extractable content for all the elements, showed again at least unimodal distribution. Sample means are also at least unimodally distributed for all elements. The outliers detected were retained in the evaluation because no technical reason to eliminate them was found.

The results were then evaluated by a one-way analysis of variance (ANOVA), which allowed the calculation of between bottle s_{bb} and within bottle s_{wb} homogeneity estimated as standard deviation, according to the following formulas:

$$s_{wb} = \sqrt{MS_{within}}$$

MS_{within} mean square within a bottle from an ANOVA

Between bottles standard deviation (s_{bb}) is given by the following equation:

$$s_{bb} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}}$$

$MS_{between}$ mean square between bottles from an ANOVA

n average number of replicates per bottle

The heterogeneity that can be hidden by method repeatability which is used as the minimum uncertainty contribution from homogeneity is defined as follows:

$$u_{bb}^{*} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}}$$

$\nu_{MSwithin}$ degrees of freedom of MS_{within}

The larger values of s_{bb} or u_{bb}^{*} are used as uncertainty contribution for homogeneity, u_{bb}.

In the case of Ni, the presence of the outlying value makes the ANOVA evaluation not appropriate and therefore an alternative approach for the estimation of the heterogeneity was

applied. Between bottles heterogeneity was modelled as rectangular distribution limited by the outlying value. The standard uncertainty using this outlier (u_{rect}) was then estimated as

$$u_{rect} = \frac{\left| \text{largest outlier - } \bar{y} \right|}{\sqrt{3}}$$

$\bar{y}$ = average of all results

The results of the homogeneity study for total and aqua regia extractable content are shown in Table 4. In most cases the uncertainty contribution for homogeneity is determined by the method repeatability.

In general, the uncertainty contributions due to homogeneity u_{bb} are below 2 %, with a few exceptions, including Ni total content (2.7 %) and Co and Zn aqua regia extractable content (2.2 % and 2.6 %, respectively).

Table 4: Results of homogeneity study

	Total content			Aqua regia extractable content		
Analyte	s_{bb} [%]	u_{bb}^* [%]	u_{bb} [%]	s_{bb} [%]	u_{bb}^* [%]	u_{bb} [%]
As	0.2	1.2	1.2	[1)]	1.6	1.6
Cd	[1)]	1.4	1.4	[1)]	1.6	1.6
Co	[1)]	0.3	0.3	[1)]	2.2	2.2
Cr	[1)]	1.4	1.4	[1)]	0.7	0.7
Cu	[1)]	0.6	0.6	[1)]	1.6	1.6
Mn	0.1	0.2	0.2	0.3	0.5	0.5
Ni	[1)]	2.6	2.7 [2)]	[1)]	0.8	0.8
Pb	0.5	0.3	0.5	0.1	0.8	0.8
Zn	[1)]	0.3	0.3	0.5	2.6	2.6

[1)] not defined due to a negative argument under the square root

[2)] estimated as rectangular distribution

5 Stability studies

5.1 Short-term stability

The short-term stability study aims to determine proper transport conditions to avoid any degradation of the material during its transport to the customer. Planning the study, the occurrence of harsh transport conditions, especially in summer time when quite high temperatures can be reached, is taken into consideration.

The short-term stability for ERM-CC141 was assessed using an isochronous design [4]. Three bottles per time and temperature were stored at 18 °C and 60 °C for 0, 1, 2 and 4 weeks, for a total of 21 bottles (only 3 bottles for t=0 weeks). The reference temperature was set to -20 °C.

Only aqua regia extractable content was tested, since potential degradation of the material is more likely to influence these parameters, rather than the total element content.

The aqua regia extractable content of the elements in the samples was analysed by ICP-OES (As, Co, Cr, Cu, Mn, Ni, Pb and Zn) and ICP-MS (Cd) (Annex 1, Table A3). The results of the measurements are shown in Annex 3.

Some outliers for Cd, Co, Ni, Pb and Zn were identified in the statistical evaluation (Grubbs test) of the data; nevertheless, as there was no technical reason to exclude them from evaluation, they remained in the data set. The data points were plotted against storage time at the test temperature and the regression line was calculated. In all cases the slope of the regression line was not found to be significantly different from zero. The results of these tests are summarised in Table 5.

Table 5: Results of the short-term stability tests

Analyte	Slope significantly different from zero at test temperature 18 °C at a level of 95% and 99% confidence	Slope significantly different from zero at test temperature 60 °C at a level of 95% and 99% confidence
As	no	no
Cd	no	no
Co	no	no
Cr	no	no
Cu	no	no
Mn	no	no
Ni	no	no
Pb	no	no
Zn	no	no

The material remained stable at 18 °C and 60 °C for up to 4 weeks. Thus, the samples can be safely dispatched under conditions where the temperatures do not exceed 60 °C for up to 4 weeks, i.e. at ambient temperature.

5.2 Long-term stability

The long-term stability is tested to establish the shelf life of the CRM. The CRM is tested over a certain period of time, from which an extrapolation for the future is calculated.

In this study, the long-term stability was also assessed only for the aqua regia extractable content (see paragraph 5.1) using an isochronous design [4]. Two bottles per time and temperature were stored at 4 °C and 18 °C for 0, 8, 12 and 24 months, for a total of 14 bottles (only 2 bottles for t=0 weeks). The reference temperature was set to –20 °C.

The aqua regia extractable content of the elements in the selected samples was analysed mainly by ICP-MS (Annex 1, Table A4), as a possible degradation of the material might influence this parameter, rather than the total element content. The long term stability plots are shown in Annex 4.

Some outliers were detected for Co, Cr, Cu, Ni, Pb and Zn in the statistical evaluation (Grubbs test) of long-term stability data. As there was no technical reason to exclude them from evaluation, they remained in the data set. The data points were plotted against time and the regression line calculated. The uncertainty of stability u_{lts} of the materials is then calculated for the required shelf life as:

$$u_{lts} = \frac{RSD}{\sqrt{\sum (t_i - \bar{t})^2}} * t$$

with *RSD* being the relative standard deviation of all results of the stability study, t_i being the time point for each replicate, $\bar{t}$ being the average of all time points and t being the proposed shelf life (36 months at 18 °C). The results are summarised in Table 6.

Table 6: Results of the long-term stability tests of 24 month-study (only aqua regia extractable content).

Analyte	Slope significantly different from zero at 4 °C at level of confidence of 95 %	Slope significantly different from zero at 18 °C at level of confidence of 95 %	u_{lts} [%] at 4 °C for shelf-life of 36 months	u_{lts} [%] at 18 °C for shelf-life of 36 months
As	no	yes	2.0	**2.5***
Cd	no	no	2.7	**3.0**
Co	no	no	1.9	**2.1**
Cr	no	no	5.1	**2.7**
Cu	no	no	2.2	**1.7**
Mn	no	no	2.4	**1.4**
Ni	no	no	2.8	**2.0**
Pb	no	no	1.1	**1.4**
Zn	no	no	0.6	**1.0**

* Including additional contribution given by the slope of the regression line

None of the elements, except As, showed a slope of the regression lines significantly different from zero. The data set for As at the test temperature of 18 °C showed a slope significantly different from zero at 18 °C at a level of confidence of 95 %. For this reason the estimate of u_{lts} uncertainty contribution for As was calculated by including degradation of the regression line [8].

With regard to Cr analyses, the uncertainty of 36 months at 18 °C is almost half of the uncertainty of 36 months at 4°C. This difference is due to an outlying value which was retained since no particular problems were evidenced. However, this difference is more likely to be due to a method artefact (ICP-MS), than a problem of material instability.

The uncertainty contribution u_{lts} was established for 36 months at 18 °C and used to calculate the overall uncertainty of the certified values.

Based on the results obtained, the storage temperature for the material was set to 18 °C.

In addition, to ensure stability beyond the initial shelf life, the material will then be subjected to IRMM's regular stability monitoring programme.

6 Characterisation study

6.1 Methods used

The characterisation assessed the total content and the aqua regia extractable content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in the soil ERM-CC141 by laboratory intercomparison. Several laboratories were selected for the characterisation campaign and they provided measurements using different procedures. A list of all the methods used in the certification of the CRM is given in Annex 1, Table A5-6.

Two of the laboratories used a modified procedure for the aqua regia extractable content different from the one prescribed in ISO 11466 [1]. In those cases, samples were treated with the aqua regia acid mixture in combination with microwave heating.

As reported by Nieuwenhuize *et al* [7] and Sastre *et al* [8], microwave digestion with aqua regia offers a good alternative to traditional reflux extraction, providing comparable and accurate results. In the present study, the aqua regia leaching results obtained for the quality control sample (BCR-141R) by using a modified procedure were found not significant different from the certified values and therefore the datasets were retained (see paragraph 6.2).

Regarding the determination of total element content, the methods used employed the use of HF in combination with microwave heating with the addition of different acid mixtures, containing HNO_3 and HCl or $HClO_4$ with or without the addition of H_3BO_3. Non-destructive methods, such as XRF and k_0-NAA were among the other methods used.

Each laboratory received two bottles of the material and was requested to provide 6 independent results (triplicate extraction per bottle), obtained on two different days. The results collected from the participating laboratories are displayed in Annex 5.

In addition, the water content had to be determined on separate sub-samples. The water content measurements had to be carried out by drying a separate sample of at least 1 g in an oven at (105 ± 2) °C until constant weight was achieved (usually for not less than 3 hours). The results were reported in mass fractions based on dry mass.

6.2 Evaluation of results

The participants received a bottle of BCR-141R as a blind sample for quality control purposes. One result had to be provided for this sample for the total and aqua regia extractable content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn. Individual results for the quality control sample are displayed in Annex 6.

The value measured in the quality control sample (BCR-141R) by the participating laboratories was compared with the certified value of the element in the material. A target of ± 15 % deviation was selected as maximum tolerable uncertainty contribution coming from the sum of all the uncertainties, in view of the high variation observed in the uncertainties reported by the several laboratories.

If the result deviated ± 15 % or more from the certified value, the data for the ERM-CC141 for the same element provided by the same laboratory was excluded, as the laboratory's performance on that analysis was considered doubtful. In addition, all the results submitted from the laboratory were excluded when the results for ≥ 50 % of all measurands were deviating ≥ 15 % from the certified value of the control sample.

In the specific case of As, since there is only an indicative value for total content given for the control sample BCR-141R, the exclusion criterion was set to ± 20 %.

After excluding some results on the base of the quality control sample performance, the remaining data were subjected to statistical outlier tests (Dixon test, Nalimov test). Based on these tests and a visual inspection of the data, some outliers could be identified. In case of suspicious data, the laboratories were contacted upon the receipt of the results and asked to check and confirm the submitted data. The outlying values were retained when no particular problems were identified. However, due to this reason, a few results are outside the expanded uncertainty range of the certified value (see Annex 5). Nevertheless they cover the certified value thus complying with the certification requirements when the method uncertainty declared by the laboratory is considered. Therefore, they are included in the final evaluation. In these specific cases, the uncertainty stated by the laboratory is reported as note in Annex 5.

In Table 7 and Table 8 the data sets that were found to be doubtful or outliers are listed, together with the action taken.

In Table 9 and Table 10, the resulting data of the characterisation study, together with the contribution to the uncertainty of the characterisation u_{char} to the certified value are shown.

Any value of the characterisation is calculated combining the data from the different laboratories, as the mean of the laboratory means of all accepted data sets.

u_{char} is estimated as the standard deviation of laboratory means divided by n number of laboratories

All results of the batch characterisation study are summarised in Annex 5.

Table 7: Total content – data sets that were found to be doubtful or outlier with the action taken. A list of the laboratories (labs) code together with the methods used is given in Annex 1

Analyte	Lab	Description of problem	Action taken
All	L2 ICP-OES/ ET-AAS L5 ICP-MS	More than 50 % of the determinations were identified as doubtful considering the labs' performance with the quality sample	Data for all the elements were excluded.
As	L7 ICP-OES L10 HR-ICP-MS	Values were identified as doubtful considering the lab's performance with the quality sample	Values for As were excluded.
Cd	L8 ICP-MS	Value was identified as doubtful considering the lab's performance with the quality sample	Value for Cd was excluded.
Co	L1 ICP-MS L6 ED-XRF L11 ICP-OES	Values were identified as doubtful considering the labs' performance with the quality sample	Values for Co were excluded.
Cr	L8 ICP-MS	Value was identified as doubtful considering the lab's performance with the quality sample	Value for Cr was excluded.
Cu	L4 ICP-MS	Value was identified as doubtful considering the lab's performance with the quality sample	Value for Cu was excluded.
	L6 ED-XRF	Value was identified as outlier using the Dixon and Nalimov t-test at 95 % confidence level.	Reviewing of the report of L6 and the measurement method, no particular problems were identified. Value for Cu was retained.
Mn	Values accepted for all the labs (except for L2 and L5)		
Ni	L3 ID-ICP-MS L8 ICP-MS	Values were identified as doubtful considering the labs' performance with the quality sample	Values for Ni were excluded.
Pb	L1 ICP-MS L8 ICP-MS L11 ICP-OES	Values were identified as doubtful considering the labs' performance with the quality sample	Values for Pb were excluded.
Zn	L3 ID-ICP-MS L4 ICP-MS	Values were identified as doubtful considering the labs' performance with the quality sample	Values for Zn were excluded.
	L9 ICP-SFMS	Value was identified as outlier using the Nalimov t-test at 95 % confidence level.	Reviewing of the report of L9 and the measurement method, no particular problems were identified. Value for Zn was retained.

Table 8: Aqua regia extractable content – data sets that were found to be doubtful or outliers with the action taken. A list of the laboratories (labs) code together with the methods used is given in Annex 1

Analyte	Lab	Description of problem	Action taken
All	L1 ICP-OES/ ICP-MS L2 ICP-OES/ ET-AAS L5 ICP-MS	More than 50 % of the determinations were identified as doubtful considering the labs' performance with the quality sample	Data for all the elements were excluded.
As	L11 ICP-MS L12 ICP-OES	Values were identified as doubtful considering the labs' performance with the quality sample	Values for As were excluded.
	L9 ICP-MS	Value was identified as outlier using the Nalimov t-test at 95 % confidence level.	Reviewing of the report of L9 and the measurement method, no particular problems were identified. Value for As was retained.
Cd	Values accepted for all the labs (except for L1, L2 and L5)		
Co	L9 ICP-MS L12 ICP-OES	Values were identified as doubtful considering the labs' performance with the quality sample	Values for Co were excluded.
	L8 ICP-MS	Value was identified as outlier using the Nalimov t-test at 95 % confidence level.	Reviewing of the report of L8 and the measurement method, no particular problems were identified. Value for Co was retained.
Cr	L8 HR-ICP-MS L12 ICP-OES	Values were identified as doubtful considering the labs' performance with the quality sample	Values for Cr were excluded.
	L9 ICP-MS	Value was identified as outlier using the Dixon and Nalimov t-test at 95 % confidence level and Nalimov at 99 %.	Reviewing of the report of L9 and the measurement method, no particular problems were identified. Value for Cr was retained.
Cu	L9 ICP-MS	Value was identified as outlier using the Dixon and Nalimov t-test at 95 % confidence level and Nalimov at 99 %.	Reviewing of the report of L9 and the measurement method, no particular problems were identified. Value for Cun was retained.
Mn	L9 ICP-MS	Value was identified as doubtful considering the labs' performance with the quality sample	Value for Mn was excluded.
	L7 ICP-OES	Value was identified as outlier using the Nalimov t-test at 95 % confidence level.	Reviewing of the report of L7 and the measurement method, no particular problems were identified. Value for Mn was retained.

Table 8-continue

Ni	L0 ICP-OES	Value was identified as outlier using the Nalimov t-test at 95 % and 99 % confidence level.	Reviewing of the report of L0 and the measurement method, no particular problems were identified. Value for Ni was retained.
Pb	L0 ICP-OES L12 ICP-OES	Values were identified as doubtful considering the labs' performance with the quality sample	Values for Pb were excluded.
Zn	L11 ICP-OES	Value was identified as doubtful considering the labs' performance with the quality sample	Value for Zn was excluded.

Table 9: Summary of data of the characterisation – total content

Analyte	Number of independent valid datasets	Mean of laboratory means [mg/kg]	u_{char} [%]
As	6	9.9	7.0
Cd	6	0.35	5.52
Co	6	8.5	1.8
Cr	9	86	3.4
Cu	8	14.4	4.5
Mn	9	464	1.3
Ni	7	26.4	2.8
Pb	6	41	3.4
Zn	8	57	2.9

Table 10 Summary of data of the characterisation – aqua regia extractable content

Analyte	Number of independent valid datasets	Mean of laboratory means [mg/kg]	u_{char} [%]
As	6	7.5	8.2
Cd	8	0.25	4.96
Co	6	7.9	4.3
Cr	7	31	4.6
Cu	9	12.4	2.6
Mn	8	387	1.5
Ni	9	21.9	2.8
Pb	7	32.2	1.3
Zn	8	50	1.8

7 Value assignment and uncertainty estimation

7.1 Certified values and uncertainties

The certified values result from the characterisation study (Table 9 and Table 10), as explained in paragraph 6.2. All the certified values reported are calculated as the mean of the different laboratory means of all the accepted data sets.

The uncertainty of the certified values contains contributions of the characterisation u_{char}, the homogeneity u_{bb} and the long-term stability u_{lts}.

The different contributions to the CRM uncertainty are combined using the following equation:

$$U_{CRM,rel} = k\sqrt{u_{bb,rel}^2 + u_{lts,rel}^2 + u_{char,rel}^2}$$

The expanded uncertainty of the certified value U_{CRM} is calculated with a coverage factor of $k = 2$, representing a level of confidence of approximately 95 %.

The certified values and uncertainties are summarised in Table 11 and Table 12.

Table 11: Summary of the certified values and uncertainties – total content

Analyte	Certified value Mass fraction [mg/kg]	$U_{CRM,rel}$ [mg/kg] $k = 2$	$u_{char,rel}$ [1)] [%]	$u_{bb,rel}$ [2)] [%]	$u_{lts,rel}$ [3)] [%]	$U_{CRM,rel}$ [%]
As	9.9	1.5	7.0	1.2	2.5	15.1
Cd	0.35	0.05	5.52	1.4	3.0	12.87
Co	8.5	0.5	1.8	0.3	2.1	5.6
Cr	86	8	3.4	1.4	2.7	9.1
Cu	14.4	1.4	4.5	0.6	1.7	9.7
Mn	464	18	1.3	0.2	1.4	3.8
Ni	26.4	2.4	2.8	2.7	2.0	8.8
Pb	41	4	3.4	0.5	1.4	7.5
Zn	57	4	2.9	0.3	1.0	6.2

[1)] Values from characterisation study (Table 9)

[2)] Values from homogeneity data (Table 4)

[3)] Values from long term stability study aqua regia extractable content (Table 6)

Table 12: Summary of the certified values and uncertainties – aqua regia extractable content

Analyte	Certified value Mass fraction [mg/kg]	$U_{CRM,rel}$ [mg/kg] $k = 2$	$u_{char,rel}$ [1)] [%]	$u_{bb,rel}$ [2)] [%]	$u_{lts,rel}$ [3)] [%]	$U_{CRM,rel}$ [%]
As	7.5	1.4	8.2	1.6	2.5	17.5
Cd	0.25	0.04	4.96	1.6	3.0	12.05
Co	7.9	0.9	4.3	2.2	2.1	10.6
Cr	31	4	4.6	0.7	2.7	10.7
Cu	12.4	0.9	2.6	1.6	1.7	7.0
Mn	387	17	1.5	0.5	1.4	4.3
Ni	21.9	1.6	2.8	0.8	2.0	7.1
Pb	32.2	1.4	1.3	0.7	1.4	4.1
Zn	50	4	1.6	2.6	1.0	6.6

[1)] Values from characterisation study (Table 9)

[2)] Values from short term stability data (see Table 4)

[3)] Values from long term stability study aqua regia extractable content (Table 6)

7.2 Additional material information

The composition of ERM-CC 141 is given in Table 13.

Table 13: Major components (expressed as mass fraction g/kg) of ERM-CC141

Major component	SiO_2	MgO	Al_2O_3	TiO_2	Fe_2O_3	P_2O_5	K_2O	Na_2O	CaO
Mass fraction [g/kg]	782.8	6.8	167.0	7.2	65.8	1.3	42.2	21.7	6.2

The determination of the major components was performed by k_0-NAA except for SiO_2 which was determined by gravimetry and P_2O_5 by spectrophotometry.

The sum of all the oxides is larger than 100 %. This is due to the measurement uncertainty for each analyte which is between 1-20 %.

The total organic carbon (TOC) was determined according to ISO 10694 procedure [5], by using a Ströhleim C-mat 5500 (combustion furnace). In this procedure the TOC is obtained by difference between the results of the measurements of TC (total carbon) and TIC (total inorganic carbon). The TC present in the samples is converted to carbon dioxide by combustion in an oxygen-containing gas flow free of carbon dioxide at 1200 °C, while the TIC is determined separately from another sub-sample by means of acidification with H_3PO_4 and purging of the released carbon dioxide and subsequent measurement of the released amount of CO_2.

The total organic carbon is 0.99 % ± 0.03 % (average content ± standard deviation) and the total inorganic carbon is < 0.01 %, based on dry mass.

The water content was determined for randomly selected bottles [2] by using two different methods: the volumetric Karl-Fischer titration and oven drying 1 g of the sample at 105 °C, until constant mass is achieved. The results obtained were comparable, 1.3 % ± 0.2 % (n=10) by volumetric Karl-Fisher titration and 1.3 % ± 0.2 % (n=4) by oven drying.

The water activity, determined using a water activity meter (Aqualab CX3, Decagon, USA), resulted to be 0.201 ± 0.003 (n=3).

In the case of water content and activity the values are expressed as average ± expanded uncertainty, with a coverage factor k=2.

8 Metrological traceability

All the determinations were carried out by laboratories with demonstrated qualification (most of the cases accredited laboratories). In all the datasets considered for the certification, the values measured in the QC sample (BCR 141R) agree with the certified values of BCR 141R, demonstrating the correctness of the calibrations and the absence of method specific bias. All the calibrants employed were either commercially available or CRMs, all traceable to the SI.

The laboratories participating in the characterisation study have also been selected such as to provide a large variety of analytical methods, sample digestion, calibration and detection methods. In this way, independence of the values from the method used is achieved.

Thus, as the certified values are averages of SI traceable results and are not affected by method common specific bias, the certified values are System of Units (SI) traceable.

9 Commutability

CRMs must exhibit a similar analytical behaviour for given methods as an ordinary laboratory sample. ERM-CC141 is a natural loam soil. The laboratories participating in the characterisation study were selected such as to provide a large variety of analytical methods, regarding digestion/extraction, calibration and detection.

The good agreement between the results obtained for the characterisation of several parameters, shows that ERM-CC141 exhibits the same behaviour as a typical laboratory sample; therefore the commutability of the materials is confirmed.

10 Instructions for use

The bottles shall be shaken for at least two minutes before opening to ensure re-homogenisation of the content.
The minimum sample intake for the measurement of the total element content is 100 mg.
The minimum sample intake for the aqua regia extractable element content, as prescribed by ISO 11466, is 3 g.

10.1 Storage conditions

Samples should be stored at +18 °C ± 5 °C in the dark. The material picks up moisture when in prolonged contact with humid air. Spoilage by moulds may occur at water contents exceeding 8 % by mass and damage the whole sample.

However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

10.2 Safety and protection of the environment

The usual laboratory safety measures apply.

10.3 Dry mass correction

The analytical sample for analysis should be taken as it is. The correction to dry mass should be made by taking a separate portion of 1 g and drying in an oven at 105 °C until constant mass is attained (successive weighings should not differ by more than 1 mg).

10.4 Use of the certified values

The main purpose of the material is to assess method performance, e.g. for checking accuracy of analytical results. As any reference material, it can also be used for control charts or validation studies.

Comparing an analytical result with the certified value

A result is unbiased if the combined uncertainty of measurement and certified value covers the difference between the certified value and the measurement result. To this end, the following steps are necessary:

1) Assessment of the measurement uncertainty: This uncertainty will depend on whether accuracy of one individual result or accuracy of a method in general is being assessed. Measurement uncertainty can be estimated from repeatability data obtained during method validation. These repeatability data do not comprise uncertainty of the calibration. This uncertainty has to be added. The uncertainty is then estimated as

$$u_{meas} = c\sqrt{u_R^2 + u_{st}^2}$$

u_{meas}	standard measurement uncertainty
c	concentration for which the uncertainty should be evaluated
u_R	relative uncertainty due to repeatability (as taken from the validation study)
u_{st}	relative uncertainty of the calibration standard (mainly purity). u_{st} can be ignored if it is < 1/3 u_R

2) Take the standard uncertainty of the certified value of the material in question (u_{CRM}), calculated as expanded standard uncertainty divided by k factor (equal to 2)

3) Combine the two uncertainties as

$$u_c = \sqrt{u_{meas}^2 + u_{CRM}^2}$$

4) The measurement result is not significantly biased if the difference between the measured result and the certified value is smaller than 2 u_c [6].

Use in quality control charts

The material can be used for quality control charts. Different CRM-units will give the same result as potential heterogeneity is included in the uncertainty of the certified values.

Use as a calibrant

Using ERM-CC141 as calibrant is not recommended. If used nevertheless, the uncertainty of the certified value shall be taken into consideration in the final estimation of measurement uncertainty.

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Annexes

Annex 1: Methods used in the certification study

Table A1: Methods used in the micro-homogeneity study

Labcode	Analytical technique	Sample pre-treatment	Calibration
9	ICP-SFMS (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn)	Digestion for As, Cd, Co, Cu, Mn Ni, Pd, Zn: sample + 7.5 mL HNO_3 + 2 mL HF + 0.5 mL HCl, microwave digestion (170 °C, 60 min), fusion for Cr: sample + lithium (100 °C), dilution with 5 % HNO_3 prior to analysis	2-points external calibration after internal normalisation; 0 and 50 µg/L (As, Cd, Co, Cr, Cu, Ni, Pb) 0 and 100 µg/L (Mn, Zn)

Table A2: Methods used in the homogeneity study

Labcode	Analytical technique	Sample pre-treatment	Calibration
7	ICP-OES (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn)	250 mg sample + 9.5 g HNO_3 + 0.5 g $HClO_4$, microwave digestion (190 °C, 10 h), dilution to 50 g with H_2O	External calibration with single element standard solution; interference corrections; 0, 0.1, 0.25 and 0.5 mg/kg (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn)

Table A3: Methods used in the short-term stability study of the aqua regia extractable content according to ISO 11466

Labcode	Analytical technique	Sample pre-treatment	Calibration
1	ICP-OES (As, Co, Cr, Cu, Mn, Ni, Pb, Zn) ICP-MS (Cd)	According to ISO 11466 electrothermal heating mantel and quick fit	Linear regression through zero with single element standard solution; 10 and 20 mg/L (As, Co, Cr, Cu, Mn, Ni, Pb, Zn) 5 and 10 mg/L (Cd)

Table A4: Methods used in the long-term stability study of the aqua regia extractable content according to ISO 11466

Labcode	Analytical technique	Sample pre-treatment	Calibration
8	HR-ICP-MS (As, Cr, Ni) ICP-MS (Cd, Co, Mn, Pb, Zn) ICP-OES (Cu)	According to ISO 11466	Linear regression with 6 calibration standards for each element, 0 to 10 µg/L (As, Cd, Co) 0 to 100 µg/L (Cr, Ni, Pb) 0 to 1 mg/L (Cu) 0 to 200 µg/L (Mn, Zn)

Table A5: Methods used in the certification study to determine the total content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn

Lab code	Analytical technique	Sample mass [mg]	Sample pre-treatment	Calibration
0	k_0-NAA (As, Co, Cr, Mn, Zn)	800	Separate sample intakes for Mn (forming short lived radioisotopes) and for As, Co, Cr and Zn (forming medium and long lived radioisotopes) were measured. Short irradiation: the samples were irradiated for 10 min and 1 spectrum per sample was taken after a few minutes of decay. Long irradiation (7 h) at least 3 spectra were collected after 1-2 days, 1 week and > 3 weeks of decay.	IRMM-530 neutron flux monitors were used to determine the neutron flux used during irradiation, NIST 1633b Coal Fly Ash was used as validation sample
1	ICP-MS	500	Digestion: sample + 5 mL HNO_3 + 2 mL HCl + 3 mL HF, microwave digestion (240 °C, 60 bar, 40 min)	Linear regression through zero with single element standard solution; 5, 20 and 500 µg/L (As, Cd, Co, Cu, Ni, Pb) 20, 80 and 200 µg/L (Cr) 100, 400 and 1000 µg/L (Mn) 10, 40 and 100 µg/L (Zn)

Table A5-continue

2	ICP-OES (As, Co, Cr, Cu, Mn, Ni, Pb, Zn) ET-AAS (Cd)	500	Digestion: sample + 8 mL HNO_3 + 5 mL HCl + 2 mL HF, first microwave digestion (160 °C in 6 min, 210 °C in 4 min and hold for 20 min, venting for 60 min), addition of 10 ml H_3BO_3, second microwave digestion (160 °C in 8 min and hold for 7 min, venting for 60 min), dilution with H_2O to 50 mL	External calibration with single element standard solution; 0, 1, 5, 10, 50 µg/L (As) 0, 1, 2, 5, 10, 50 µg/L (Cd) 0, 1, 5, 10, 20, 50 µg/L (Co) 0, 100, 250, 500, 1000 µg/L (Cr) 0, 10, 20, 50, 100, 250 µg/L (Cu) 0, 100, 250, 500, 1000, 2000 µg/L (Mn) 0, 10, 50, 100, 250, 500 µg/L (Ni) 0, 10, 20, 50, 100 µg/L (Pb) 0, 100, 250, 500, 1000 µg/L (Zn)
3	ID-ICP-MS (Cd, Cr, Cu, Ni, Pb, Zn)	200	Sample spiked with a solution of enriched isotopes of each of the metals, Digestion: sample/spike blend + 6 mL HNO_3 + 2 mL HCl + 2 mL HF, closed microwave digestion (500 W for 7 min, 5 min hold, 1000 W for 60 min, 20 min cool down, max. pressure 30 bar), dilution with high purity water to app. 50 g	Isotopically enriched materials were used to prepare the spike solution: ^{111}Cd (96.50 %), ^{53}Cr (95.74 %), ^{65}Cu (91.2 %), ^{61}Ni (94.91 %), ^{206}Pb (92.1497 %), ^{67}Zn (93.11 %); Independent standards prepared from pure materials were used for quality control purpose.
4	ICP-MS (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn)	300	Digestion: sample + 2 mL HNO_3 + 6 mL HCl+ 2 mL HF, microwave digestion (200 °C, 75 bar, 75 min)	External calibration with single element standard solution; 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 50 and 100 µg/L
5	ICP-MS	500	Digestion: sample + 8 mL HNO_3 + 5 mL HCl + 2 mL HF, first microwave digestion (160 °C in 6 min, 210 °C in 4 min and hold for 20 min, venting for 60 min), addition of 10 ml H_3BO_3, second microwave digestion (160 °C in 8 min and hold for 7 min, venting for 60 min), dilution with H_2O to 50 mL	External calibration with single element standard solution; 0, 100, 200, 400, 600, 800, 1000 µg/L (As, Co, Cr, Cu, Ni, Pb, Zn) 0, 1, 2, 3 µg/L (Cd) 0, 0.5, 1, 1.5, 2, 2.5, 5, 10 mg/L (Mn)

Table A5-continue

6	ED-XRF (As, Co, Cr, Cu, Mn, Ni, Pb and Zn)	10000	XRF: sample + 10 % wax, homogenised by shaking, pressed to a pellet (40 mm in diameter) in a metal disc under a pressure of 25 ton	XRF: calibration with ca. 40 reference materials (geological and soil)
7	ICP-OES (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn)	200	Digestion: sample + 9.5 g HNO_3 + 0.5 g $HClO_4$, microwave digestion (190 °C, 10 h), dilution to 50 g with H_2O	External calibration with single element standard solution, interference corrections; 0, 0.1, 0.25 and 0.5 mg/kg (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn)
8	ICP-MS (As, Cd, Co, Cr, Cu, Ni, Pb) ICP-OES (Mn, Zn)	500	Digestion: sample + 10 mL HNO_3 + 8 mL HF, microwave digestion (280 °C, 260 bar, 180 min), addition of H_3BO_3 after digestion	2-points external calibration; 0 and 100 µg/L (As, Cd, Co, Cr, Cu, Ni, Pb) 0 and 500 µg/L (Mn, Zn)
9	ICP-SFMS	200	Digestion for As, Cd, Co, Cu, Ni, Pd, Zn: sample + 7.5 mL HNO_3 + 2 mL HF + 0.5 mL HCl, microwave digestion (170 °C, 60 min), fusion for Cr and Mn: sample + lithium (100 °C), dilution with 5 % HNO_3 prior to analysis	2-points external calibration after internal normalisation; 0 and 50 µg/L (As, Cd, Co, Cr, Cu, Ni, Pb) 0 and 100 µg/L (Mn, Zn)
10	HR-ICP-MS (As, Cd, Co, Pb) ICP-OES (Cr, Cu, Mn, Ni, Zn)	100	Digestion: sample + 4 mL HNO_3 + 1mL HF + 2 mL HCl, first closed microwave digestion (100 W for 1 min, 500 W in 5 min and hold for 10 min, 1000 W in 5 min and hold for 45 min, 0 W in 1 min, cooling for 15 min), adding 5 mL H_3BO_3, second closed microwave digestion (1400 W in 5 min and hold for 15 min, cooling for 15 min), dilution with H_2O to 30 mL	Linear regression with calibration solutions; 0, 0.05, 0.1, 0.25, 0.5, 1, 2, 5 and 10 µg/L (As) 0, 0.2, 0.5, 1, 2, 5 and 10 µg/L (Cd, Co, Pb) 0.25, 5, 10, 25, 50, 100, 250, 500 and 1000 µg/L (Cr, Cu, Mn, Ni, Zn)

Table A5-continue

11	ICP-OES (Co, Cr, Cu, Mn, Ni, Pb, Zn)	200	Digestion for Co, Cu, Ni, Pd, Zn: sample + 7.5 mL HNO_3 + 2 mL HF + 0.5 mL HCl, microwave digestion (170 °C, 60 min), fusion for Cr and Mn: sample + lithium (100 °C), dilution with 10 % HNO_3 prior to analysis	2-points external calibration after internal normalisation; 0 and 10 mg/L (As, Cd, Co, Cu, Mn, Ni, Pb, Zn)

Table A6: Methods used in the certification study to determine the aqua regia extractable content according to ISO 11466

Lab code	Analytical technique	Sample pre-treatment	Calibration
0	ICP-OES (Cr, Cu, Mn, Ni, Pb, Zn)	According to ISO 11466 Leaching apparatus from Gerhardt (15 min 105 °C, 15 min 190 °C, 120 min 190 °C, 1 h cooling	Linear regression with single element standard solution; 0.1, 0.2, 0.5, 2.5, 5, 7.5 mg/L
1	ICP-OES (As, Co, Cr, Cu, Mn, Ni, Pb, Zn) ICP-MS (Cd)	According to ISO 11466 electrothermal heating mantel and quick fit	Linear regression through zero with single element standard solution; 10 and 20 mg/L (As, Co, Cr, Cu, Mn, Ni, Pb, Zn) 5 and 10 mg/L (Cd)
2	ICP-OES (As, Co, Cr, Cu, Mn, Ni, Pb, Zn) ET-AAS (Cd)	According to ISO 11466	External calibration with single element standard solution; 0, 10, 20, 50, 100 µg/L (As) 0, 0.2, 0.5, 1, 2, 5, 10 µg/L (Cd) 0, 10, 20, 50, 100, 250, 500, 1000 µg/L (Co, Cr, Cu, Ni, Pb, Zn) 0, 10, 20, 50, 100, 250, 500, 1000, 3000 µg/L (Mn)
4	ICP-MS (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn)	According to ISO 11466 Gerhardt Kjeldatherm leaching temperature 140 °C	External calibration with single element standard solution; 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 µg/L (As) 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10 µg/L (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn)
5	ICP-MS	According to ISO 11466	External calibration with single element standard solution; 0, 100, 250, 500, 1000, 1500, 2000 µg/L (As, Co, Cr, Cu, Mn, Ni, Pb, Zn) 0, 1, 2, 3 µg/L (Cd)

Table A6-continue

6	ICP-OES (As, Co, Cr, Cu, Mn, Ni, Pb, Zn) ET-AAS (Cd)	According to ISO 11466 Gerhardt Kjeldatherm leaching temperature 140 °C	External calibration with single element standard solution; 20, 40, 100, 200, 500, 1000, 1500 µg/L (As) 0.1, 0.2, 0.4, 0.6, 1, 1.5, 2 µg/L (Cd) 4, 8, 20, 40, 100, 200 µg/L (Co) 4.8, 12, 24, 48, 120, 240, 600, 1200, 1800 µg/L (Cr) 16, 40, 80, 160, 400, 800, 2000, 4000, 6000 µg/L (Cu) 0.2, 0.4, 1, 2, 5, 10 mg/L (Mn) 8, 20, 40, 80, 200, 400, 1000, 2000 µg/L (Ni) 1, 2, 4, 6, 10, 15, 20 µg/L (Pb) 0.08, 0.2, 0.4, 0.8, 2, 4, 10 mg/L (Zn)
7	ICP-MS (As, Cd, Co, Cr, Cu, Ni, Pb) ICP-OES (Mn, Zn)	According to ISO 11466	Linear regression with calibration solutions; 0, 100 µg/L (As, Cd, Co, Cr, Cu, Ni, Pb) 0, 500 µg/L (Mn, Zn)
8	HR-ICP-MS (As, Cr, Ni) ICP-MS (Cd, Co, Mn, Pb, Zn) ICP-OES (Cu)	According to ISO 11466	Linear regression with 6 calibration standards for each element; 0 to 10 µg/L (As, Cd, Co) 0 to 100 µg/L (Cr, Ni, Pb) 0 to 1 mg/L (Cu) 0 to 200 µg/L (Mn, Zn)
9	ICP-MS	According to ISO 11466 Barnstead Electrothermal Thermomantel, Afterwards the digest was diluted	Linear regression with single element standard solution; 0, 20, 40, 100 µg/L (As) 0, 2, 4, 10 µg/L (Cd) 0, 40, 80, 200 µg/L (Co, Cr, Cu, Ni, Pb) 0, 400, 800, 2000 µg/L (Mn) 0, 100, 200, 500 µg/L (Zn)
10	ICP-SFMS	According to ISO 11466 CEM Mars 5 MW, 120 °C, ramp 60 min, hold 120 min	2-points external calibration after internal normalisation; 0, 50 µg/L (As, Cd, Co, Cr, Cu, Ni, Pb) 0, 100 µg/L (Mn, Zn)

Table A6-continue

11	DCR-ICP-MS* (As) HR-ICP-MS (Cd, Co, Pb) ICP-OES (Cr, Cu, Mn, Ni, Zn)	According to ISO 11466 leaching temperature 95 ℃	External calibration with single- and multi-element standard solution; 0, 0.05, 0.1, 0.25, 0.5, 1, 2, 5, 10 µg/L (As) 0, 0.2, 0.5, 1, 2, 5, 10 µg/L (Cd, Co, Pb) 0.25, 5, 10, 25, 50, 100, 250, 500, 1000 µg/L (Cr, Cu, Mn, Ni, Zn)
12	ICP-OES	According to ISO 11466 CEM Mars 5 MW, 120 ℃, ramp 60 min, hold 120 min	2-points external calibration after internal normalisation; 0, 10 mg/L (As, Cd, Co, Cu, Mn, Ni, Pb, Zn)

* DCR (Dynamic Reaction Cell) with a O_2 gas mode (0.55 mL/min) was used for As measurement

Annex 2: Homogeneity study

Table A7: Homogeneity data for As. Mass fraction in mg/kg on dry mass basis

Short Term Stability				Homogeneity test			
Bottle No.	Replicate 1	Replicate 2	Replicate 3	Bottle No.	Replicate 1	Replicate 2	Replicate 3
74	7.6	7.1	7.9	192	7.3	7.9	8.3
343	7.9	7.6	7.6	362	8.1	7.9	8.1
511	7.8	7.2	8.5	795	7.6	8.3	7.9
799	7.7	7.1	6.5	945	8.1	8.0	8.2
924	8.0	7.9	7.2	1108	8.2	7.7	7.9
1037	7.6	7.7	7.4	1587	7.3	8.3	8.4
1195	7.9	7.4	6.6	1760	7.8	7.8	7.3
1369	7.5	7.2	6.8	1958	8.2	7.5	8.3
1442	7.7	7.1	7.6	2043	7.6	8.2	7.8
1488	7.3	7.7	7.1	2388	8.2	7.6	8.0
1629	7.7	8.2	6.6	2765	7.7	7.9	8.8
1872	7.6	7.5	7.4	3054	8.1	8.4	8.2
2541	7.5	8.2	7.6	3381	7.6	7.6	7.3
2762	7.6	6.9	6.8	3435	7.8	7.7	7.2
2849	7.8	7.1	7.0	3783	8.0	7.7	8.7
3027	7.8	7.2	7.3	4081	7.9	7.8	8.1
3253	7.7	6.9	6.8				
3639	7.6	7.3	8.0				
3854	7.4	7.2	7.5				
3984	7.7	7.2	7.0				
4067	7.2	7.6	7.8				

Table A8: Homogeneity data for Cd. Mass fraction in mg/kg on dry mass basis

Short Term Stability				Homogeneity test			
Bottle No.	Replicate 1	Replicate 2	Replicate 3	Bottle No.	Replicate 1	Replicate 2	Replicate 3
74	0.24	0.24	0.25	192	0.41	0.42	0.40
343	0.22	0.25	0.30	362	0.37	0.45	0.42
511	0.25	0.24	0.26	795	0.38	0.43	0.44
799	0.26	0.24	0.24	945	0.39	0.42	0.44
924	0.27	0.26	0.24	1108	0.42	0.41	0.41
1037	0.25	0.25	0.27	1587	0.41	0.41	0.40
1195	0.25	0.24	0.24	1760	0.40	0.43	0.44
1369	0.25	0.24	0.24	1958	0.45	0.40	0.44
1442	0.25	0.25	0.24	2043	0.44	0.42	0.40
1488	0.27	0.24	0.24	2388	0.41	0.43	0.43
1629	0.25	0.23	0.24	2765	0.41	0.41	0.42
1872	0.25	0.25	0.25	3054	0.41	0.42	0.41
2541	0.25	0.23	0.24	3381	0.44	0.39	0.42
2762	0.28	0.28	0.24	3435	0.39	0.42	0.42
2849	0.25	0.28	0.24	3783	0.37	0.39	0.42
3027	0.24	0.26	0.24	4081	0.41	0.41	0.42
3253	0.25	0.24	0.24				
3639	0.24	0.28	0.26				
3854	0.27	0.24	0.24				
3984	0.25	0.25	0.25				
4067	0.25	0.23	0.25				

Table A9: Homogeneity data for Co. Mass fraction in mg/kg on dry mass basis

Short Term Stability				Homogeneity test			
Bottle No.	Replicate 1	Replicate 2	Replicate 3	Bottle No.	Replicate 1	Replicate 2	Replicate 3
74	7.8	7.9	8.3	192	8.0	8.1	8.0
343	7.9	7.9	8.1	362	8.0	8.0	7.8
511	7.9	7.8	8.1	795	8.0	8.1	8.1
799	7.8	7.7	7.9	945	8.0	7.9	8.1
924	7.8	7.6	8.3	1108	8.0	7.9	8.1
1037	7.7	8.1	8.1	1587	8.0	7.9	8.1
1195	7.4	8.4	7.6	1760	8.0	8.2	8.0
1369	7.8	8.1	7.7	1958	7.9	8.0	8.1
1442	7.8	8.0	7.8	2043	8.0	8.0	8.1
1488	7.2	8.0	7.4	2388	8.0	8.0	8.1
1629	8.1	7.6	7.3	2765	7.9	7.9	8.1
1872	7.5	10.7	8.3	3054	7.9	8.0	8.0
2541	7.5	7.9	8.2	3381	8.1	8.0	8.0
2762	7.6	7.8	7.6	3435	8.0	7.9	8.0
2849	7.5	8.0	7.2	3783	8.0	7.9	7.9
3027	8.2	7.7	9.1	4081	8.0	8.1	7.9
3253	11.0	8.1	7.6				
3639	9.5	8.1	7.7				
3854	7.4	7.9	8.3				
3984	7.7	8.1	7.6				
4067	7.6	7.9	8.3				

Table A10: Homogeneity data for Cr. Mass fraction in mg/kg on dry mass basis

Short Term Stability				Homogeneity test			
Bottle No.	Replicate 1	Replicate 2	Replicate 3	Bottle No.	Replicate 1	Replicate 2	Replicate 3
74	54	51	54	192	71	66	72
343	52	52	52	362	72	67	71
511	53	50	53	795	67	69	68
799	54	50	53	945	66	67	72
924	52	52	52	1108	72	73	72
1037	53	51	53	1587	66	67	72
1195	53	52	51	1760	68	82	68
1369	53	51	53	1958	65	71	70
1442	53	52	53	2043	68	74	69
1488	53	50	51	2388	66	71	68
1629	53	53	52	2765	71	75	66
1872	52	52	53	3054	65	67	65
2541	51	52	53	3381	66	69	65
2762	52	49	51	3435	67	67	75
2849	51	51	51	3783	66	68	69
3027	54	51	53	4081	73	66	69
3253	52	51	52				
3639	55	51	56				
3854	52	51	53				
3984	54	51	52				
4067	53	51	53				

Table A11: Homogeneity data for Cu. Mass fraction in mg/kg on dry mass basis

Short Term Stability				Homogeneity test			
Bottle No.	Replicate 1	Replicate 2	Replicate 3	Bottle No.	Replicate 1	Replicate 2	Replicate 3
74	10	10	11	192	14	14	14
343	11	10	11	362	14	14	14
511	11	10	11	795	14	14	14
799	10	10	10	945	14	14	14
924	11	11	10	1108	14	14	14
1037	11	10	11	1587	14	14	14
1195	10	10	10	1760	14	16	14
1369	10	11	10	1958	14	14	14
1442	11	10	11	2043	14	14	14
1488	10	10	10	2388	14	14	14
1629	11	11	10	2765	14	14	14
1872	10	11	10	3054	14	14	14
2541	10	11	10	3381	14	14	14
2762	11	10	10	3435	14	14	14
2849	11	10	10	3783	14	14	14
3027	11	10	10	4081	14	14	14
3253	10	10	10				
3639	10	10	13				
3854	10	10	10				
3984	11	10	10				
4067	10	10	11				

Table A12: Homogeneity data for Mn. Mass fraction in mg/kg on dry mass basis

Short Term Stability				Homogeneity test			
Bottle No.	Replicate 1	Replicate 2	Replicate 3	Bottle No.	Replicate 1	Replicate 2	Replicate 3
74	401	383	400	192	436	441	431
343	386	389	392	362	433	438	429
511	388	383	395	795	435	439	437
799	397	375	401	945	437	434	437
924	382	380	391	1108	433	430	436
1037	391	389	395	1587	435	430	434
1195	385	399	389	1760	435	438	433
1369	394	392	395	1958	431	433	436
1442	396	392	386	2043	434	436	435
1488	375	390	386	2388	437	434	442
1629	387	368	381	2765	431	428	440
1872	386	387	399	3054	431	434	431
2541	385	385	392	3381	437	435	437
2762	377	383	392	3435	434	431	429
2849	378	391	380	3783	434	430	431
3027	389	377	385	4081	431	439	431
3253	395	391	390				
3639	385	392	378				
3854	385	380	392				
3984	396	387	384				
4067	392	383	400				

Table A13: Homogeneity data for Ni. Mass fraction in mg/kg on dry mass basis

Short Term Stability				Homogeneity test			
Bottle No.	Replicate 1	Replicate 2	Replicate 3	Bottle No.	Replicate 1	Replicate 2	Replicate 3
74	22	21	22	192	25	25	25
343	22	21	24	362	25	25	25
511	21	21	22	795	25	25	25
799	21	20	21	945	25	24	25
924	21	22	21	1108	25	24	25
1037	21	21	22	1587	24	24	25
1195	21	21	21	1760	25	40	25
1369	22	21	21	1958	24	25	25
1442	21	21	22	2043	25	25	28
1488	22	21	21	2388	24	25	25
1629	22	22	21	2765	24	24	25
1872	21	21	22	3054	24	25	24
2541	21	22	22	3381	25	24	25
2762	22	20	21	3435	25	24	24
2849	22	22	21	3783	24	24	24
3027	22	21	22	4081	24	25	24
3253	21	21	21				
3639	23	21	22				
3854	21	21	22				
3984	21	21	21				
4067	21	21	22				

Table A14: Homogeneity data for Pb. Mass fraction in mg/kg on dry mass basis

Short Term Stability				Homogeneity test			
Bottle No.	Replicate 1	Replicate 2	Replicate 3	Bottle No.	Replicate 1	Replicate 2	Replicate 3
74	30	29	31	192	34	33	33
343	29	29	31	362	33	33	33
511	29	28	30	795	33	33	33
799	29	28	29	945	34	33	33
924	28	29	30	1108	33	33	33
1037	30	28	31	1587	33	33	33
1195	29	29	29	1760	33	33	33
1369	29	28	29	1958	33	33	33
1442	30	29	30	2043	33	33	33
1488	29	29	28	2388	33	33	33
1629	30	30	29	2765	33	33	33
1872	31	29	29	3054	33	33	33
2541	28	29	30	3381	33	33	33
2762	29	28	29	3435	33	33	32
2849	28	29	28	3783	33	32	32
3027	30	29	29	4081	33	33	33
3253	28	29	29				
3639	30	29	30				
3854	29	28	30				
3984	29	29	29				
4067	29	29	30				

Table A15: Homogeneity data for Zn. Mass fraction in mg/kg on dry mass basis

Short Term Stability				Homogeneity test			
Bottle No.	Replicate 1	Replicate 2	Replicate 3	Bottle No.	Replicate 1	Replicate 2	Replicate 3
74	50	47	50	192	52	51	51
343	49	48	80	362	52	51	51
511	49	46	50	795	52	51	51
799	49	47	49	945	51	51	51
924	48	49	49	1108	51	51	51
1037	49	47	50	1587	51	51	52
1195	49	48	47	1760	51	52	50
1369	49	47	49	1958	51	52	51
1442	49	48	49	2043	51	51	51
1488	49	47	47	2388	51	51	51
1629	49	49	48	2765	50	51	51
1872	49	47	49	3054	51	51	51
2541	48	49	50	3381	51	51	51
2762	48	46	48	3435	51	51	51
2849	48	47	47	3783	51	50	50
3027	50	47	49	4081	51	52	51
3253	48	47	48				
3639	51	47	66				
3854	48	47	49				
3984	49	47	48				
4067	49	47	50				

Annex 3: Short-term stability study

Error bars are single standard deviations

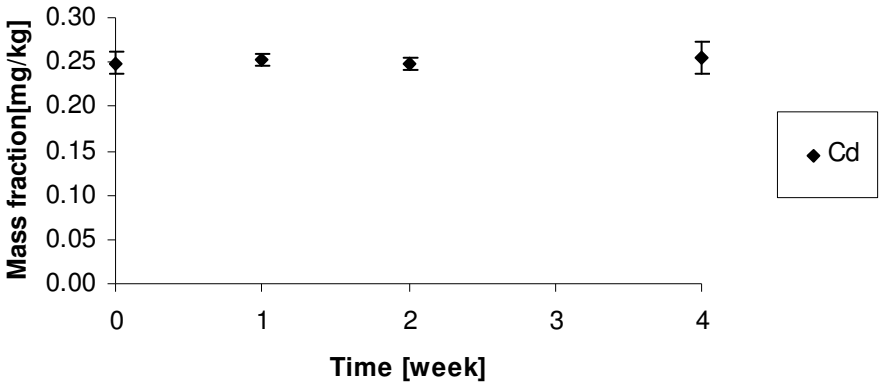

Figure A1: Short-term stability graph for aqua regia extractable Cd at 18 °C

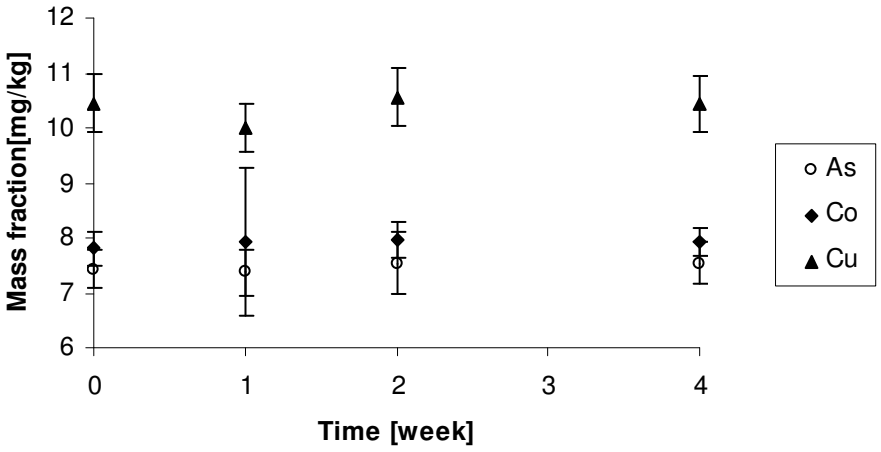

Figure A2: Short-term stability graph for aqua regia extractable As, Co and Cu at 18 °C

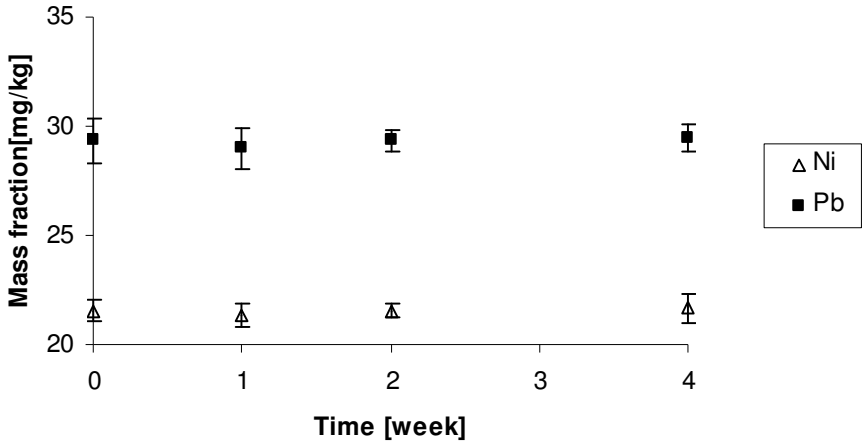

Figure A3: Short-term stability graph for aqua regia extractable Ni and Pb at 18 °C

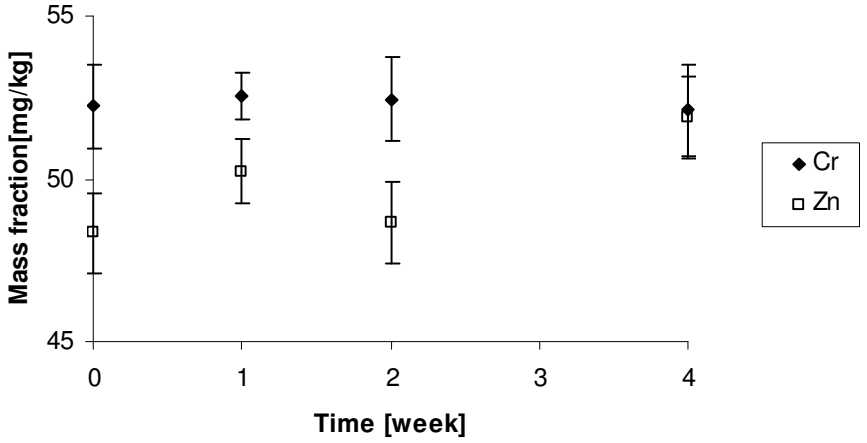

Figure A4: Short-term stability graph for aqua regia extractable Cr and Zn at 18 °C

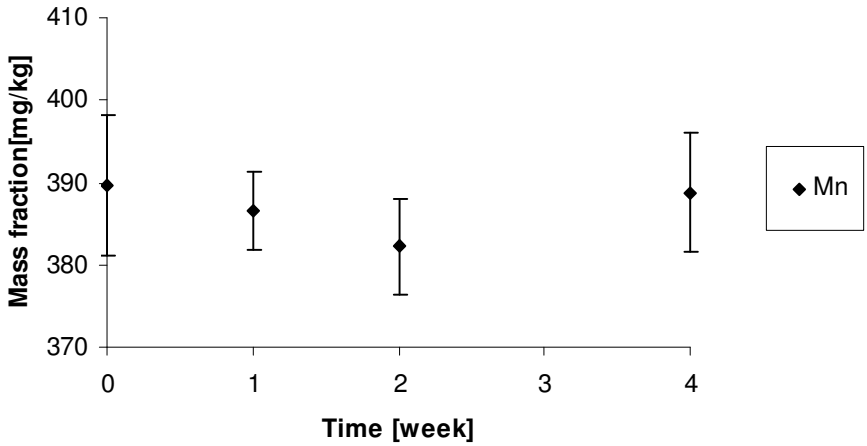

Figure A5: Short-term stability graph for aqua regia extractable Mn at 18 °C

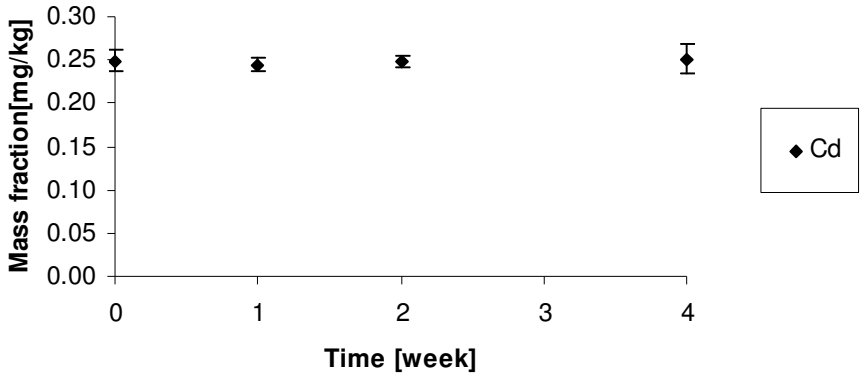

Figure A6: Short-term stability graph for aqua regia extractable Cd at 60 °C

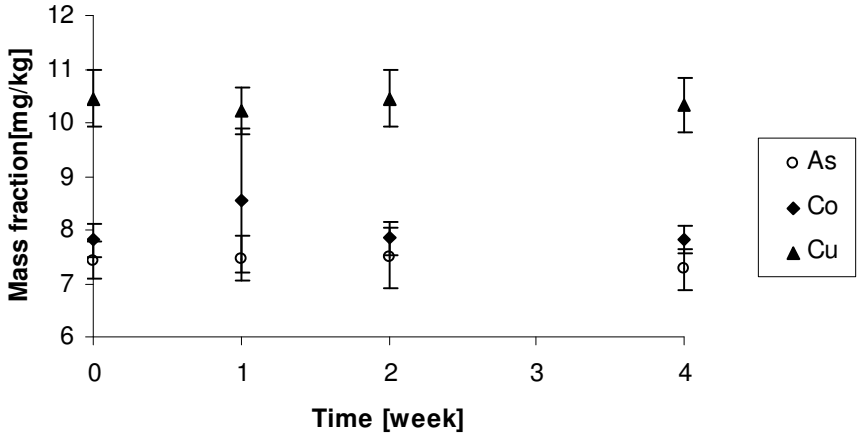

Figure A7: Short-term stability graph for aqua regia extractable As, Co and Cu at 60 °C

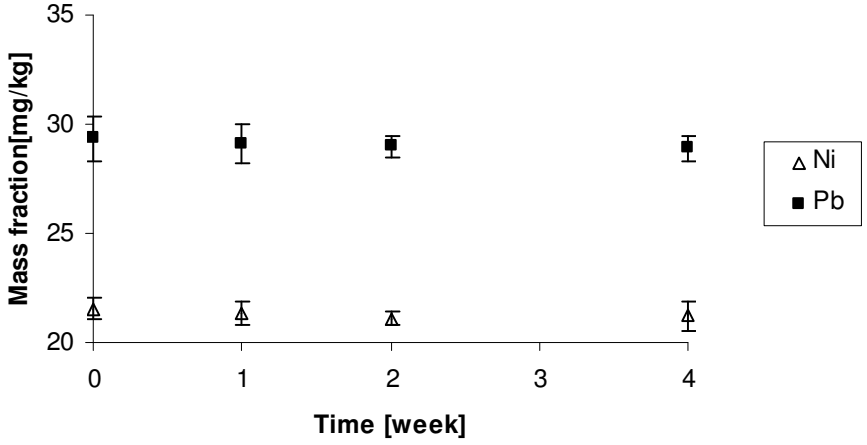

Figure A8: Short-term stability graph for Ni and aqua regia extractable Pb at 60 °C

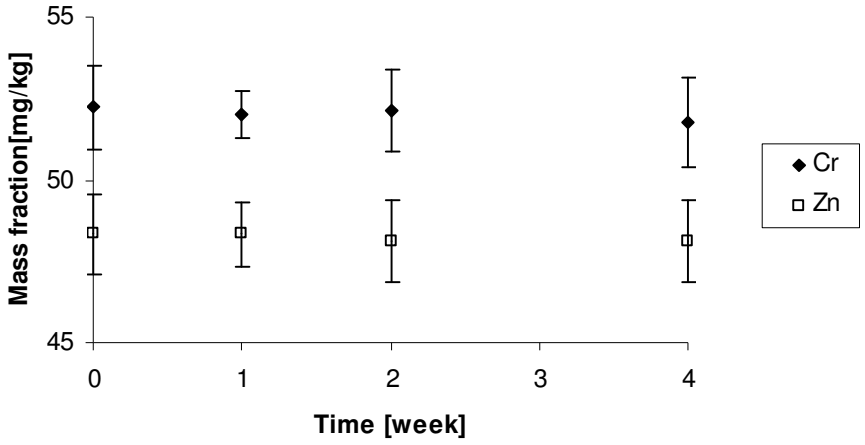

Figure A9: Short-term stability graph for aqua regia extractable Cr and Zn at 60 °C

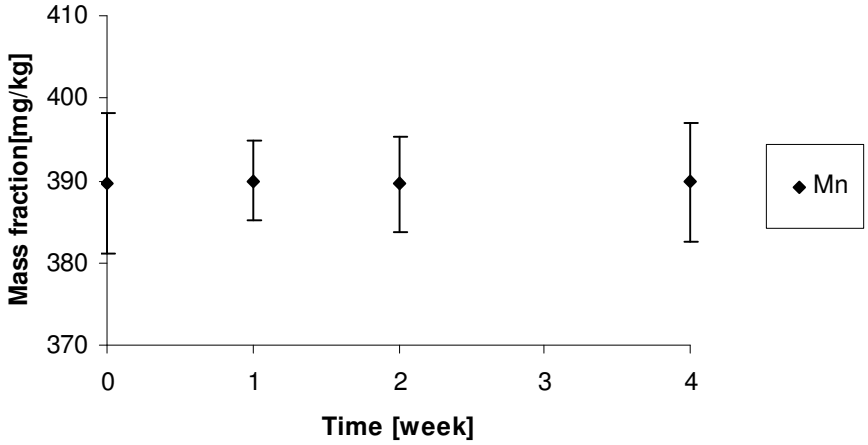

Figure A10: Short-term stability graph for aqua regia extractable Mn at 60 °C

Annex 4: Long-term stability study

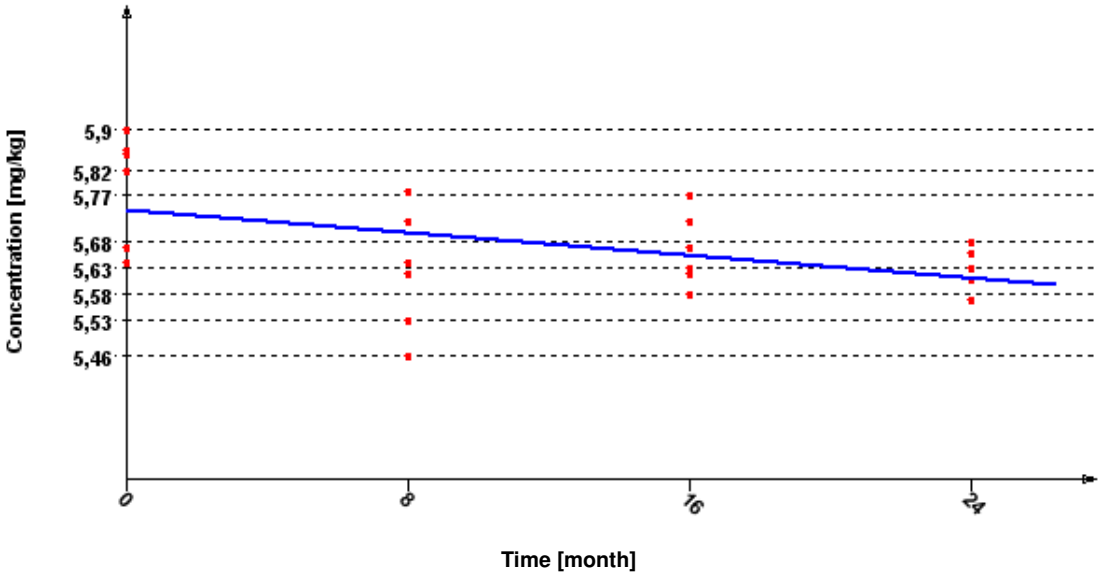

Figure A11: Long-term stability graph for aqua regia extractable As at 18 °C

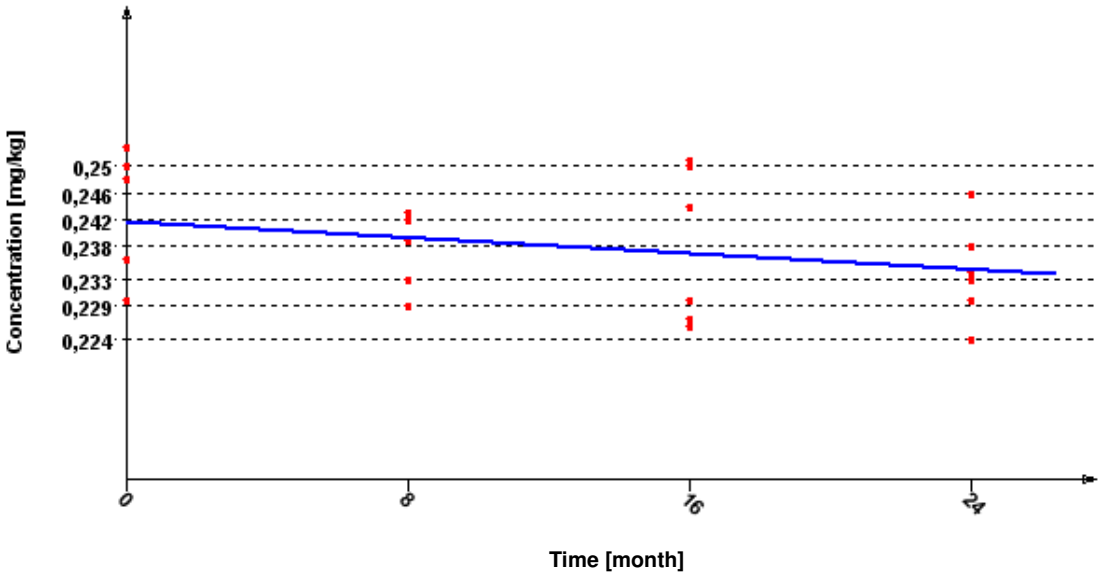

Figure A12: Long-term stability graph for aqua regia extractable Cd at 18 °C

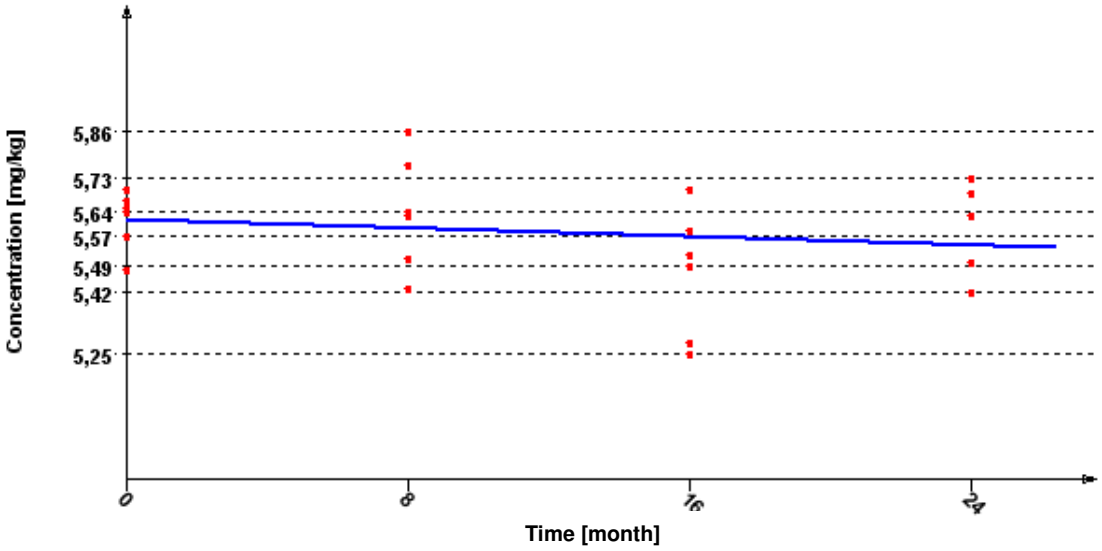

Figure A13: Long-term stability graph for aqua regia extractable Co at 18 °C

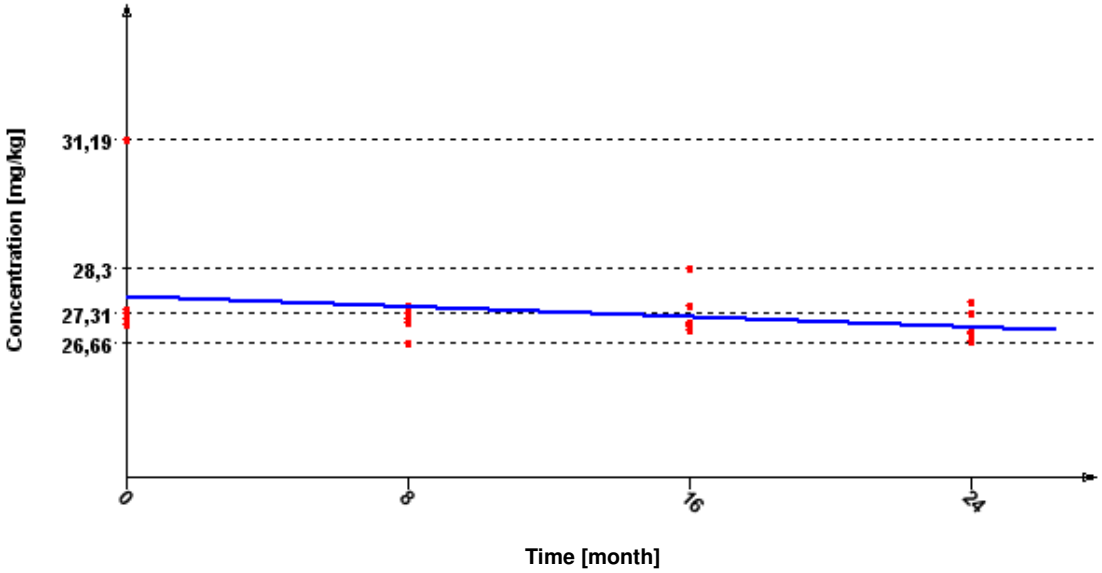

Figure A14: Long-term stability graph for aqua regia extractable Cr at 18 °C

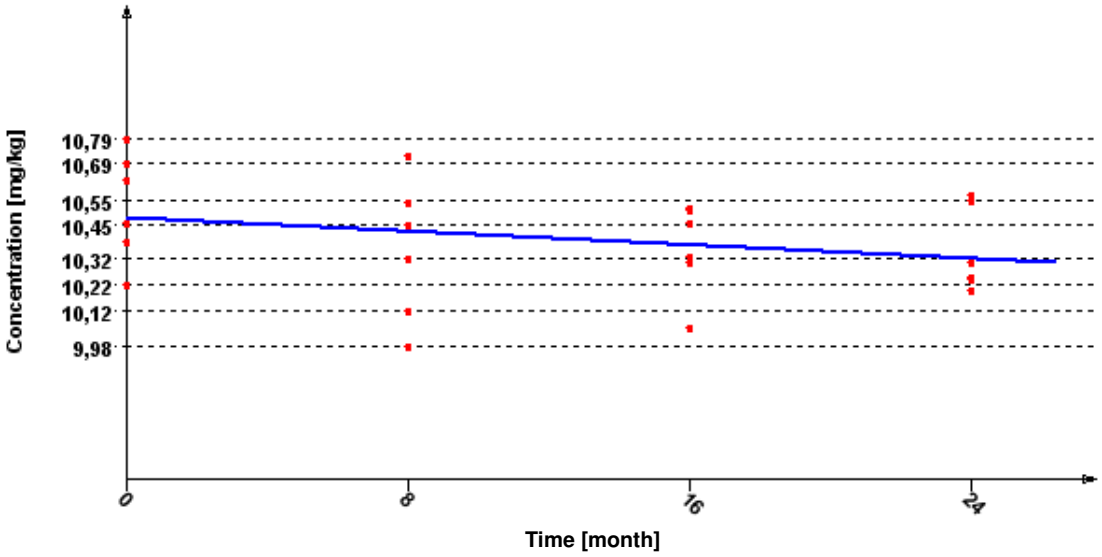

Figure A15 Long-term stability graph for aqua regia extractable Cu at 18 °C

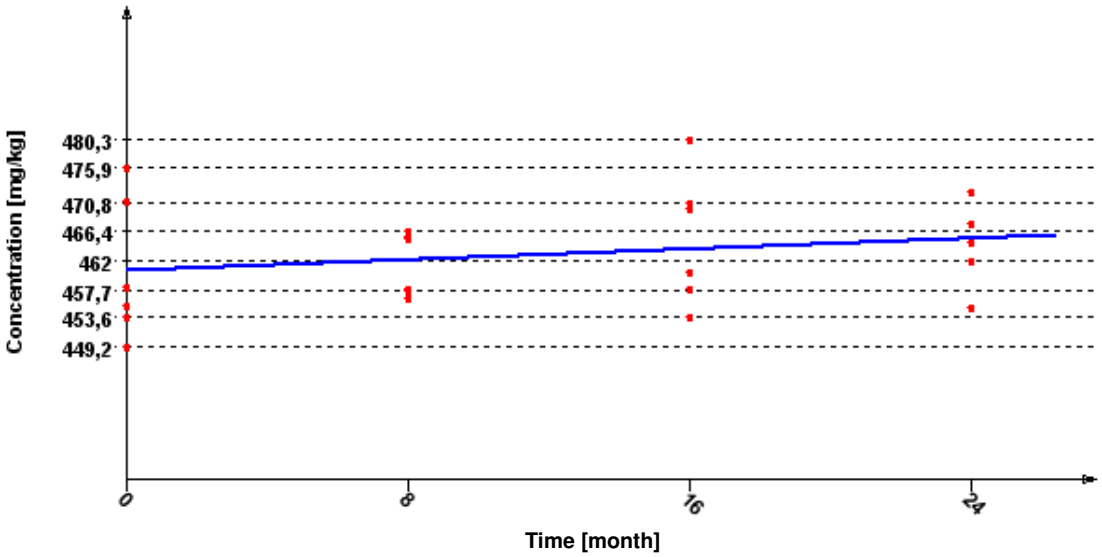

Figure A16: Long-term stability graph for aqua regia extractable Mn at 18 °C

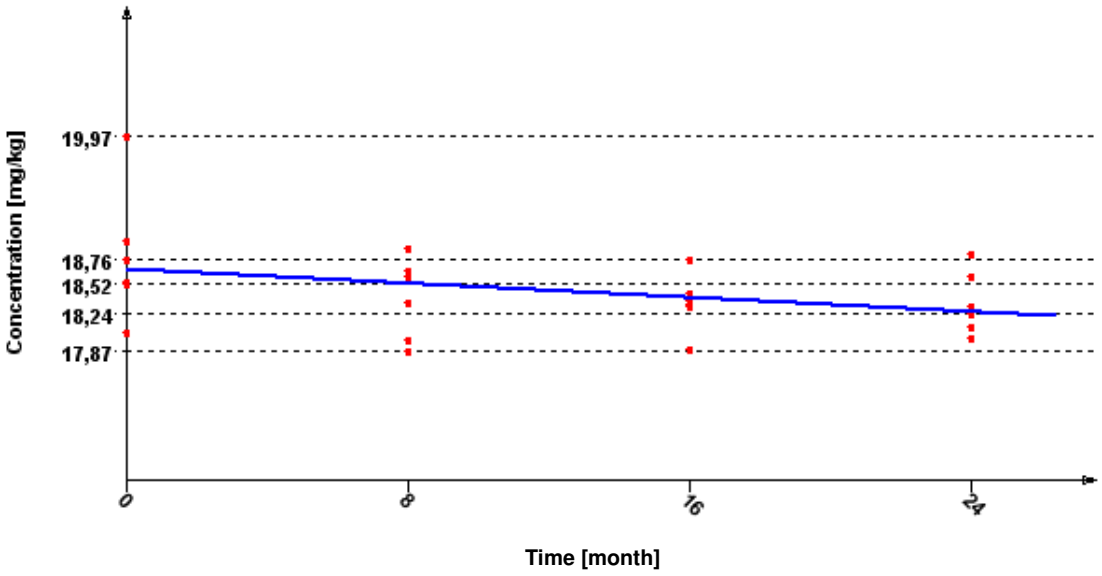

Figure A17: Long-term stability graph for aqua regia extractable Ni at 18 °C

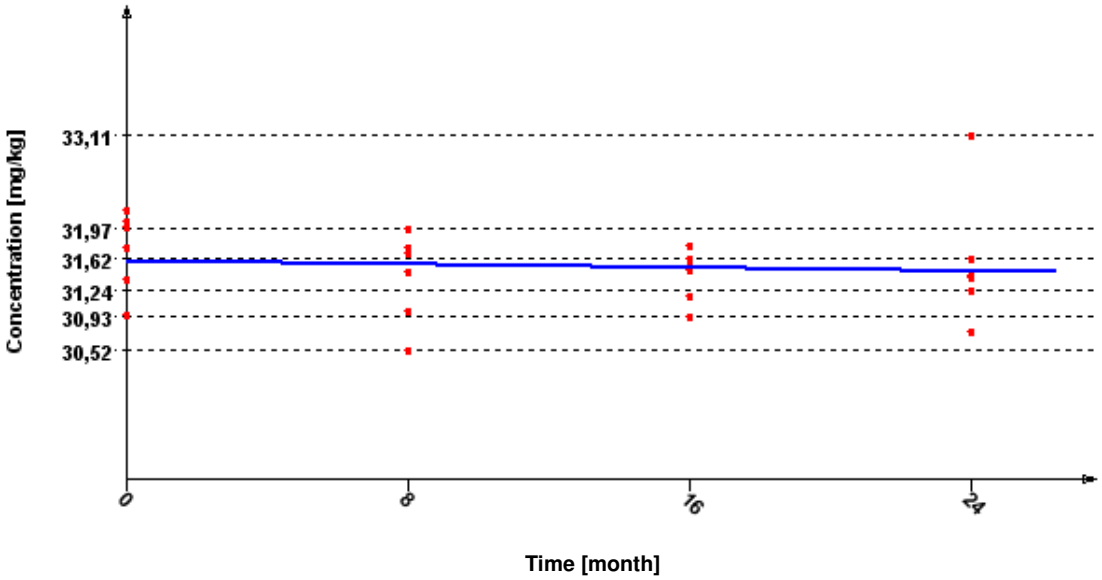

Figure A18: Long-term stability graph for aqua regia extractable Pb at 18 °C

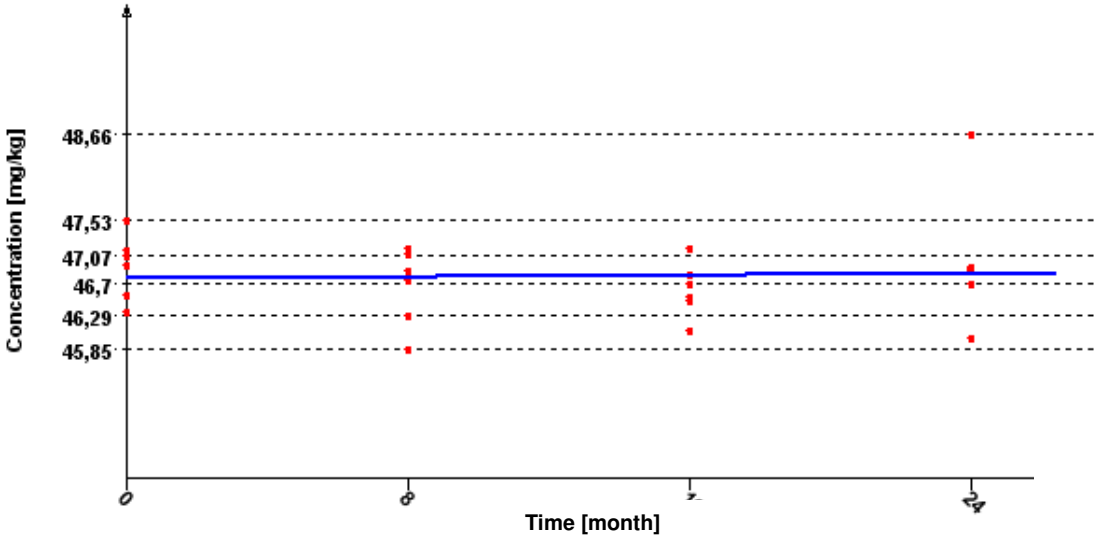

Figure A19: Long-term stability graph for aqua regia extractable Zn at 18 °C

Annex 5: Data from the certification study

Total content

The uncertainty stated by the laboratory is reported as note.

Table A16: Individual results as reported for the total content of As (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - k_0-NAA	9.46	9.41	9.42	9.45	9.36	9.41	9.42	0.04
1 - ICP-MS	9.0	9.0	9.0	9.0	9.0	9.0	9.0	0.0
4 - ICP-MS	10.6	11.2	11.1	11.3	11.2	11.7	11.2	0.4
6 - ED-XRF	6.7	7.9	7.8	7.3	7.9	7.8	7.6	0.5
8 - ICP-MS	10.9	10.2	9.0	8.6	9.6	9.3	9.6	0.8
9 - ICP-SFMS	12.1	12.2	12.9	11.9	12.6	12.6	12.4	0.4

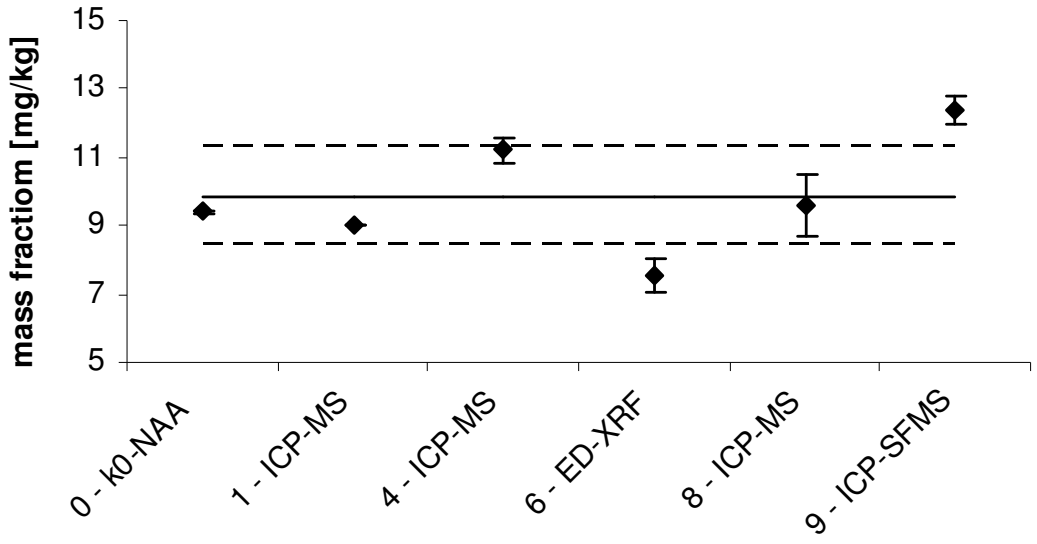

Figure A20: Results for the total content of As as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab6 (ED-XRF) = 1.4 mg/kg, Lab9 (ICP-SFMS) = 2.1 mg/kg

Table A17: Individual results as reported for the total content of Cd (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
1 - ICP-MS	0.5	0.4	0.3	0.5	0.3	0.3	0.4	0.1
3 - ID-ICP-MS	0.330	0.325	0.335	0.335	0.324	0.333	0.330	0.005
4 - ICP-MS	0.32	0.31	0.32	0.31	0.33	0.32	0.32	0.01
7 - ICP-OES	0.46	0.30	0.37	0.29	0.35	0.35	0.35	0.06
9 - ICP-SFMS	0.28	0.31	0.30	0.28	0.31	0.29	0.30	0.01
10 - HR-ICP-MS	0.44	0.44	0.42	0.43	0.42	0.42	0.43	0.01

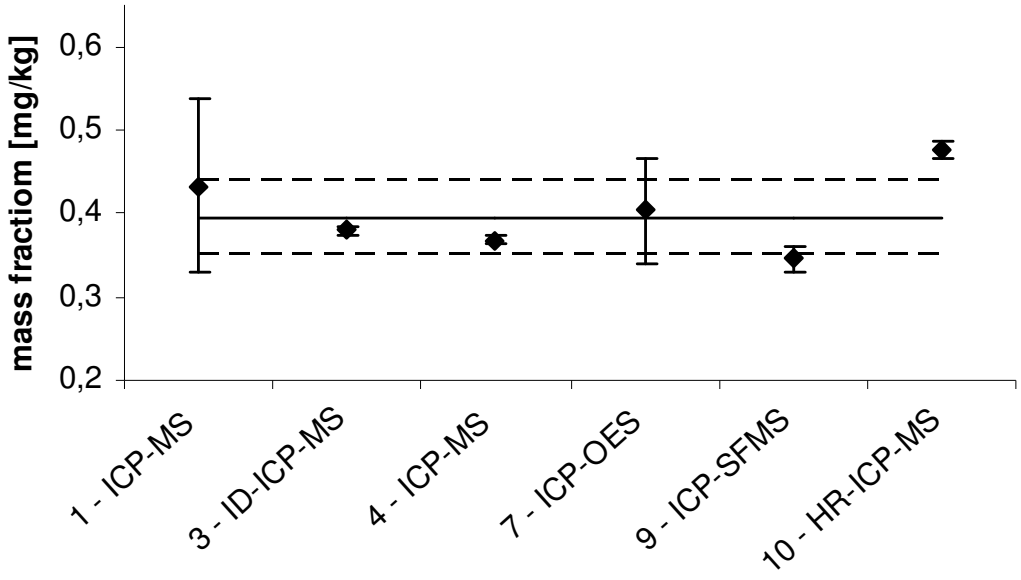

Figure A21: Results for the total content of Cd as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab10 (HR-ICP-MS) = 5%

Table A18: Individual results as reported for the total content of Co (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - k_0-NAA	8.41	8.37	8.46	8.55	8.47	8.31	8.43	0.08
4 - ICP-MS	7.0	7.8	8.3	7.4	8.58	8.6	7.9	0.6
7 - ICP-OES	8.2	8.6	8.4	8.6	8.2	8.1	8.4	0.2
8 - ICP-MS	9.0	8.9	8.6	8.7	8.4	8.4	8.7	0.2
9 - ICP-SFMS	9.1	9.4	8.8	9.2	9.0	9.0	9.1	0.2
10 - HR-ICP-MS	8.9	8.2	8.4	8.0	8.2	8.4	8.4	0.3

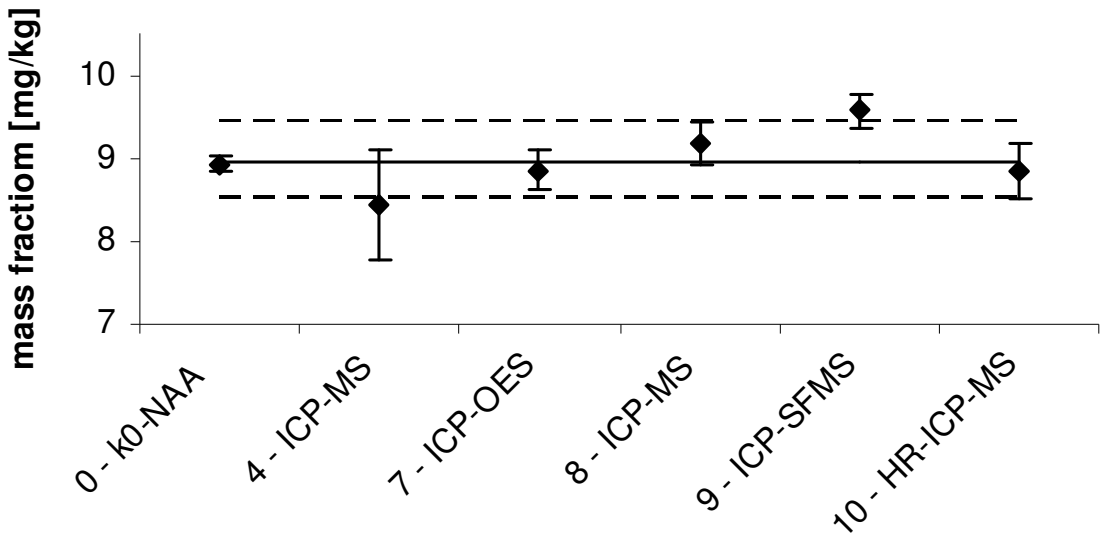

Figure A22: Results for the total content of Co as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Table A19: Individual results as reported for the total content of Cr (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - k_0-NAA	94.5	96.5	95.5	96.5	97.8	94.3	95.5	1.1
1 - ICP-MS	77	85	83	83	81	67	79	7
3 - ID-ICP-MS	77.1	87.4	81.2	73.1	87.4	83.2	81.6	5.7
4 - ICP-MS	69.4	79.2	76.9	74.2	78.4	82.9	76.8	4.6
6 - ED-XRF	82.9	81.5	91.6	86.2	90.2	98.9	88.6	6.4
7 - ICP-OES	71	76	76	79	71	80	76	4
9 - ICP-SFMS	102	92	97	100	93	99	97	4
10 - ICP-OES	82.6	78.6	84.5	79.6	82.7	85.3	82.2	2.7
11 - ICP-OES	102	92	97	100	93	99	97	4

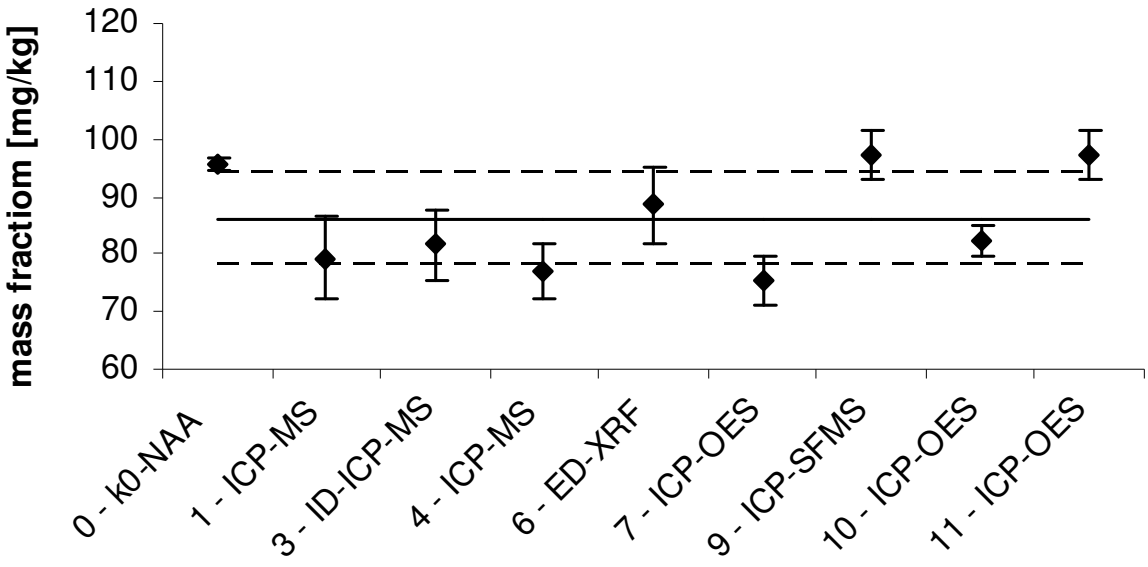

Figure A23: Results for the total content of Cr as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Table A20: Individual results as reported for the total content of Cu (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
1 - ICP-MS	15.0	14.0	14.0	15.0	14.0	14.0	14.3	0.5
3 - ID-ICP-MS	14.7	14	13.8	14.2	14.8	14.2	14.3	0.4
6 - ED-XRF	15.6	19.1	16.6	17.6	20.4	18.5	18.0	1.7
7 - ICP-OES	14.1	14.3	14.3	14.5	14.1	14.4	14.3	0.2
8 - ICP-MS	16.3	15.6	13.7	13.5	14.4	13.6	14.5	1.2
9 - ICP-SFMS	15.1	15.1	15.2	15.5	14.5	15.5	15.2	0.4
10 - ICP-OES	13.6	14.1	13.3	14.0	13.6	13.3	13.7	0.3
11 - ICP-OES	11.5	11.2	11.5	11.3	11.2	11.1	11.3	0.2

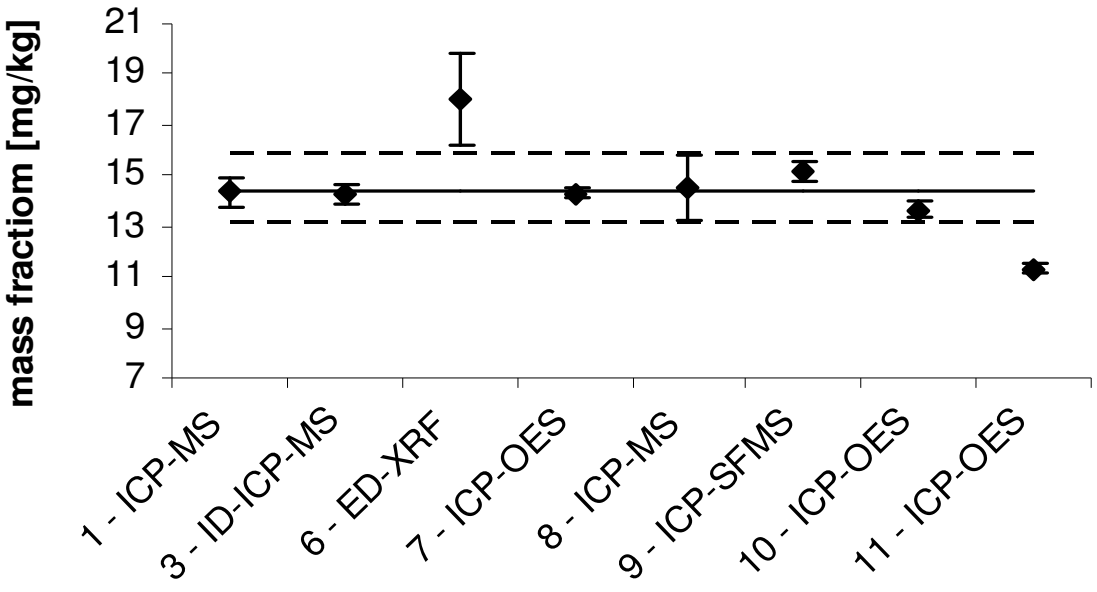

Figure A24: Results for the total content of Cu as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab6 (ED-XRF) = 6.5 mg/kg, Lab 11 (ICP-OES) = 1.5 mg/kg

Table A21: Individual results as reported for the total content of Mn (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - k_0-NAA	489.7	487	483.6	489.7	491.4	489	488.4	2.8
1 - ICP-MS	459	465	452	470	447	405	450	23
4 - ICP-MS	480.5	511.3	488.9	500.3	477.5	478.0	489.4	13. 8
6 - ED-XRF	460	448	460	441	450	453	452	7
7 - ICP-OES	450.4	449	455	449.4	450.2	447.8	450.3	2.5
8 - ICP-OES	433	455	460	461	463	458	455	11
9 - ICP-SFMS	470	468	471	469	469	469	469	1
10 - ICP-OES	455.7	435.6	443.7	430.2	443.3	438.6	441.2	8.8
11 - ICP-OES	470	478	481	476	480	476	477	4

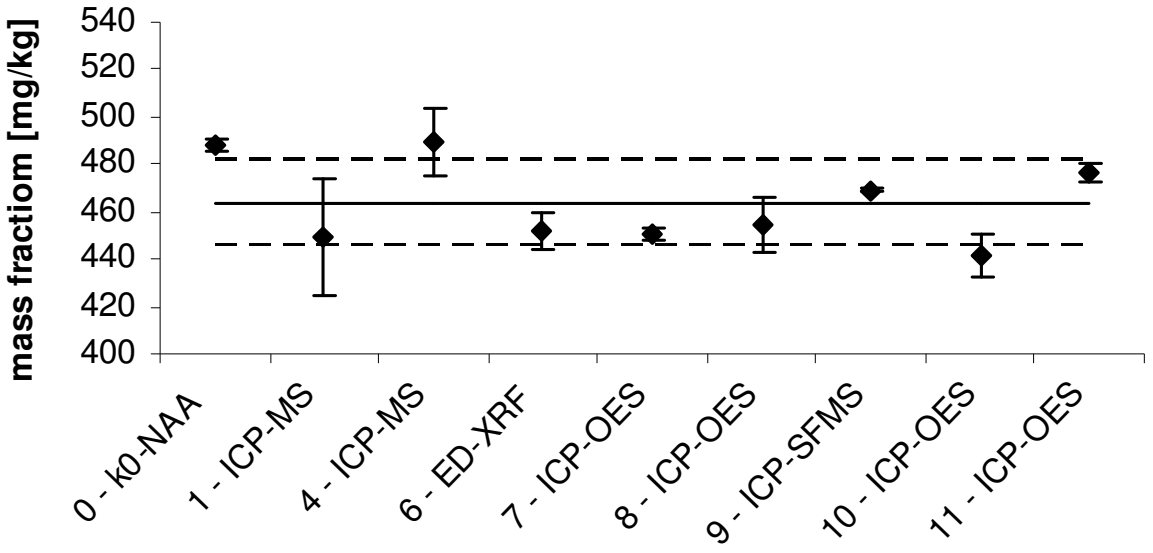

Figure A25: Results for the total content of Mn as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value. ----: expanded uncertainty of the certified value)

Note: Lab0 (k_0-NAA) = 23.0 mg/kg

Table A22: Individual results as reported for the total content of Ni (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
1 - ICP-MS	26	25	25	25	24	24	25	1
4 - ICP-MS	21.6	22.6	24.7	22.4	24.7	25.5	23.6	1.6
6 - ED-XRF	27.2	30.1	25.4	27.7	26.5	29.9	27.8	1.9
7 - ICP-OES	28.5	28.4	28.4	28.5	27.7	27.7	28.2	0.4
9 - ICP-SFMS	29.4	29.4	28.8	28.7	28.4	28.7	28.9	0.4
10 - ICP-OES	28	26	25	25	26	27	26	1
11 - ICP-OES	24.2	26.8	24.7	25.7	24.9	24.7	25.2	0.9

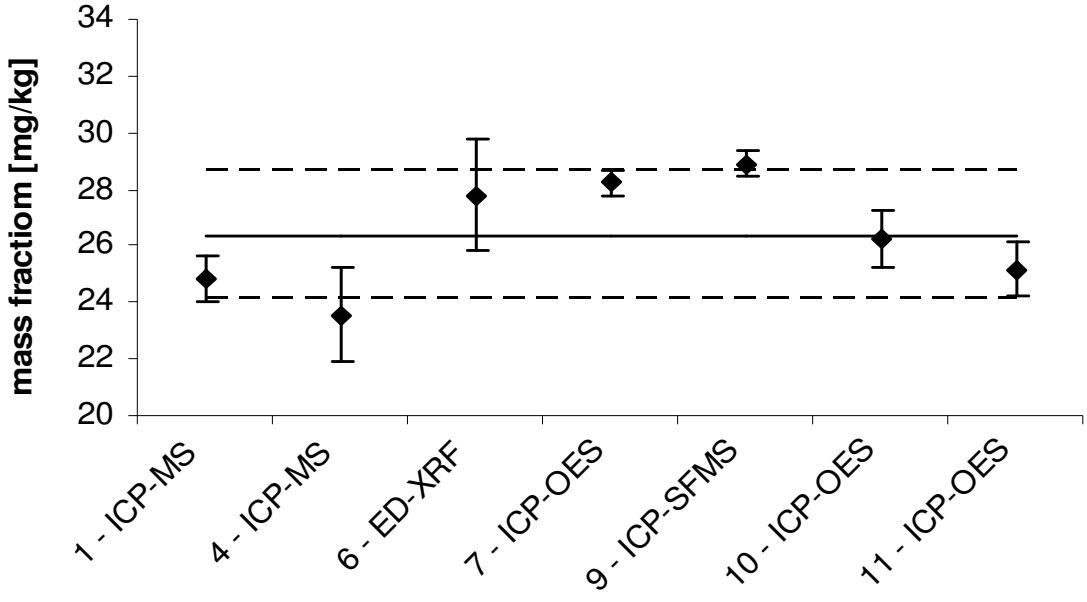

Figure A26: Results for the total content of Ni as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value. ----: expanded uncertainty of the certified value)

Table A23: Individual results as reported for the total content of Pb (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
3 - ID-ICP-MS	40.4	40.0	40.0	40.0	40.1	39.9	40.1	0.2
4 - ICP-MS	40	41	41	42	42	41	41	1
6 - ED-XRF	42.3	38.9	38.9	38.8	38.6	38.6	39.4	1.4
7 - ICP-OES	38.0	37.6	35.0	36.5	35.0	36.7	36.5	1.3
9 - ICP-SFMS	45.1	45.0	46.2	44.3	44.1	46.0	45.1	0.9
10 – HR-ICP-MS	46.2	45.8	46.9	43.3	45.3	45.0	45.4	1.2

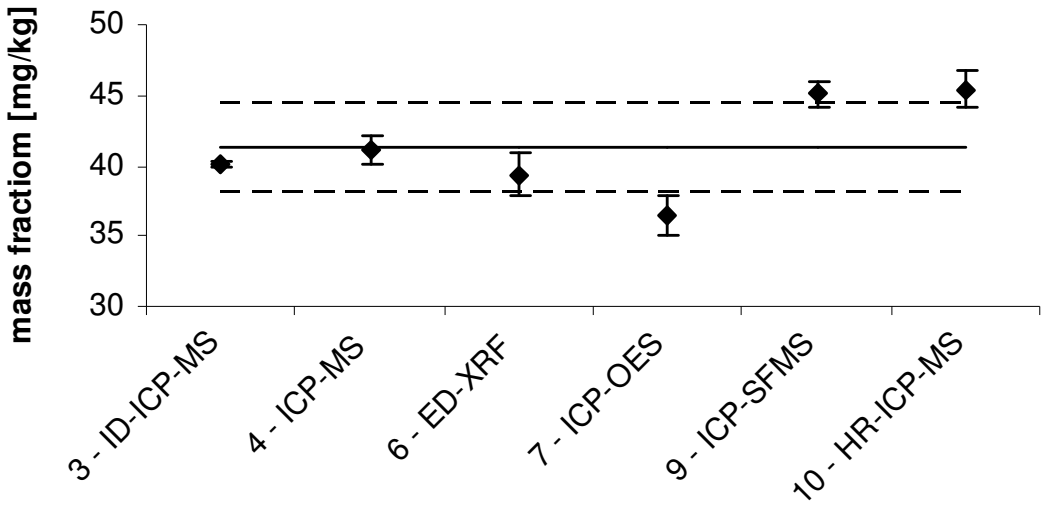

Figure A27: Results for the total content of Pb as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value. ----: expanded uncertainty of the certified value)

Note: Lab7 (ICP-OES) = 13.3 mg/kg

Table A24: Individual results as reported for the total content of Zn (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - k_0-NAA	58.6	60.4	57.8	58.7	59.7	57.4	58.8	1.1
1 - ICP-MS	54	52	54	52	53	54	53	1
6 - ED-XRF	56	56	58	55	57	56	56	1
7 - ICP-OES	53.2	52.9	53.9	53.6	53.6	53.7	53.5	0.4
8 - ICP-MS	51.2	53.5	52.3	55.2	55.6	54.8	53.8	1.8
9 - ICP-SFMS	66.2	67.7	64.1	66.3	67.3	63.6	65.9	1.7
10 - ICP-OES	54.5	55.6	54.7	52.0	53.3	55.5	54.3	1.4
11 - ICP-OES	61.5	62.0	63.4	62.5	62.3	63.5	62.5	0.8

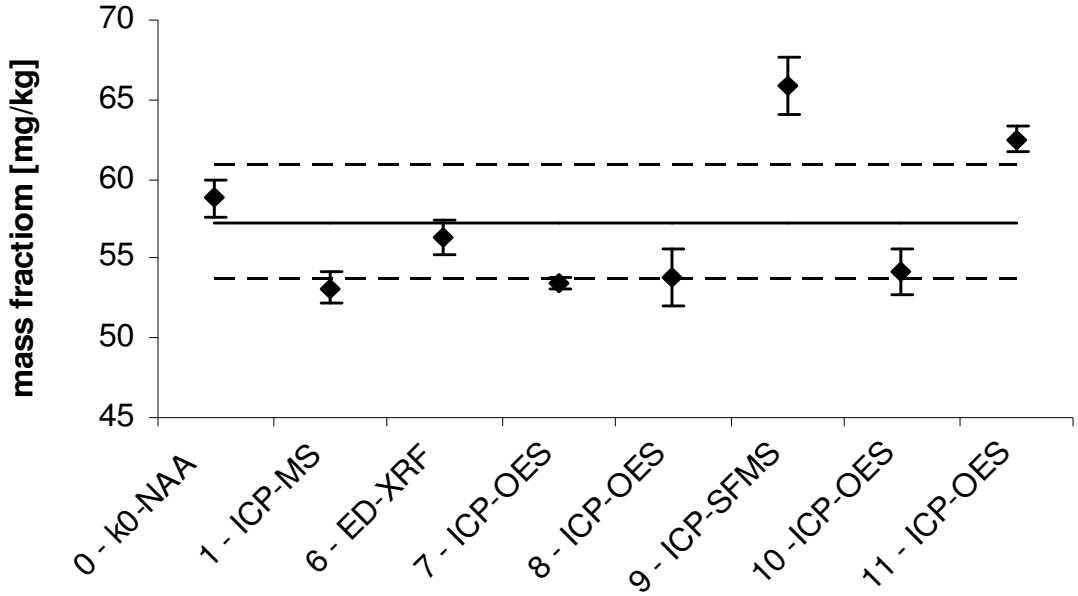

Figure A28: Results for the total content of Zn as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value. ----: expanded uncertainty of the certified value)

Note: Lab9 (ICP-SFMS) = 8.3 mg/kg, Lab 11 (ICP-OES) = 7.3 mg/kg

Aqua regia extractable content

The uncertainty stated by the laboratory is reported as note.

Table A25: Individual results as reported for the aqua regia extractable content of As (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
4 - ICP-MS	7.5	7.5	6.8	7.4	7.0	7.1	7.2	0.3
6 - ICP-OES	8.2	8.6	8.2	7.8	8.4	8.2	8.2	0.3
7 - ICP-MS	9.9	10.1	9.3	8.7	8.7	9.1	9.3	0.6
8 – HR-ICP-MS	9.0	8.4	7.6	8.3	8.3	7.9	8.2	0.5
9 - ICP-MS	4.9	4.5	4.9	5.1	4.8	5.0	4.9	0.2
10 - ICP-SFMS	7.0	6.5	7.2	7.2	7.1	7.5	7.1	0.3

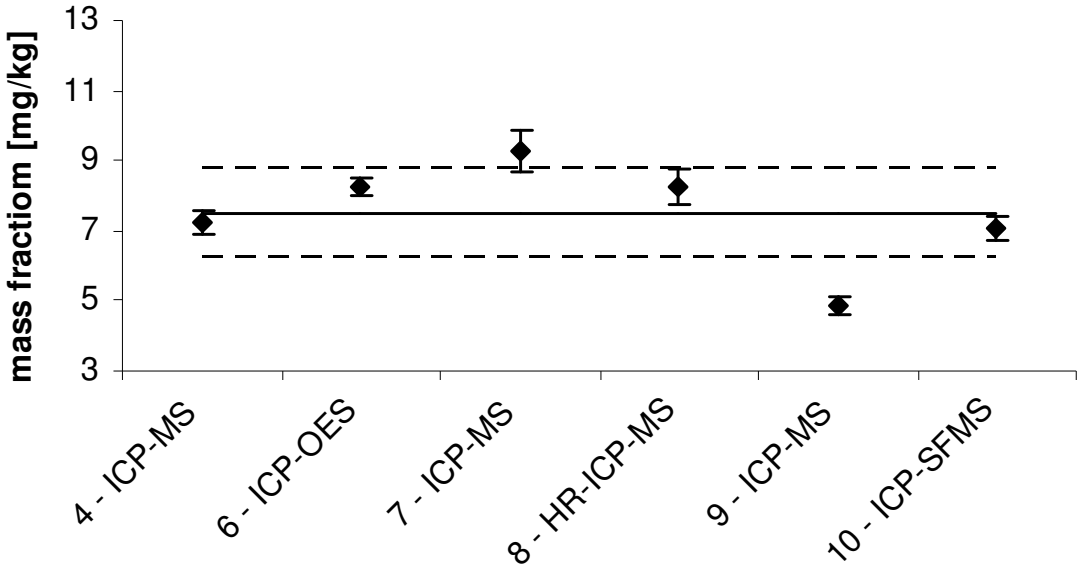

Figure A29: Results for the aqua regia extractable content of As as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab9 (ICP-MS) = 20 %

Table A26: Individual results as reported for the aqua regia extractable content of Cd (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
4 - ICP-MS	0.28	0.28	0.28	0.28	0.26	0.26	0.27	0.01
6 - ET-AAS	0.23	0.23	0.24	0.24	0.24	0.24	0.24	0.01
7 - ICP-MS	0.29	0.28	0.25	0.28	0.29	0.28	0.28	0.01
8 - ICP-MS	0.20	0.17	0.21	0.24	0.22	0.18	0.20	0.03
9 - ICP-MS	0.24	0.24	0.23	0.24	0.23	0.23	0.24	0.01
10 - ICP-SFMS	0.27	0.24	0.27	0.24	0.26	0.25	0.26	0.01
11 - HR-ICP-MS	0.31	0.33	0.31	0.30	0.31	0.33	0.31	0.01
12 - ICP-OES	0.25	0.23	0.21	0.19	0.22	0.22	0.22	0.02

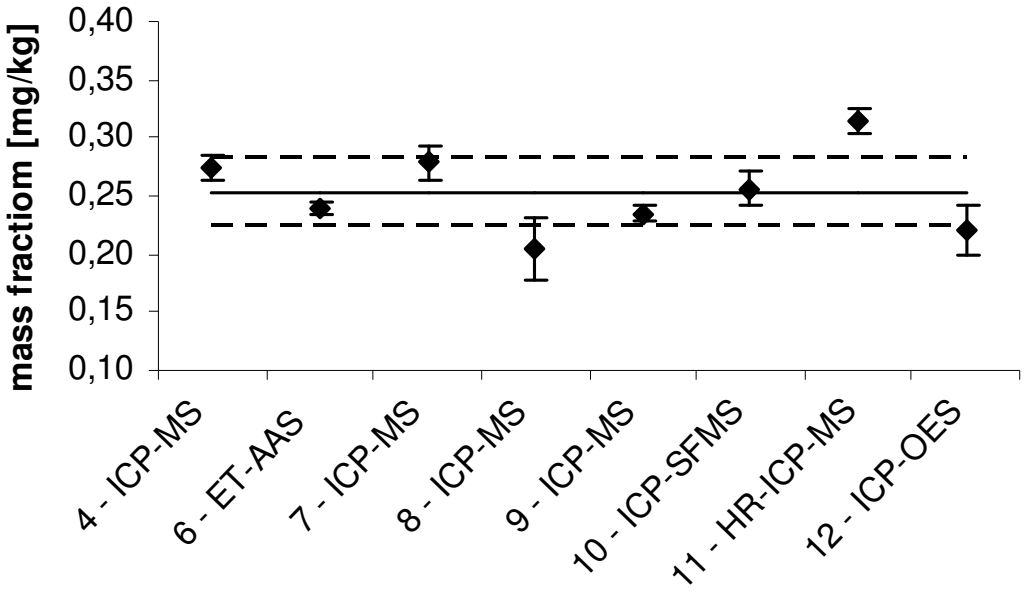

Figure A30: Results for the aqua regia extractable content of Cd as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab 11 (HR-ICP-MS) = 5%

Table A27: Individual results as reported for the aqua regia extractable content of Co (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
4 - ICP-MS	7.2	7.5	8.2	7.1	7.8	8.0	7.6	0.4
6 - ICP-OES	7.9	8.1	7.8	7.8	8.0	8.2	8.0	0.2
7 - ICP-MS	8.8	8.8	8.9	9.0	9.0	9.0	8.9	0.1
8 - ICP-MS	6.6	6.5	6.4	6.7	6.4	6.2	6.5	0.2
10 - ICP-SFMS	8.1	7.4	7. 8	7.4	7.6	7.9	7.7	0.3
11 - HR-ICP-MS	8.4	8.4	8.6	8.3	8.4	8.4	8.4	0.1

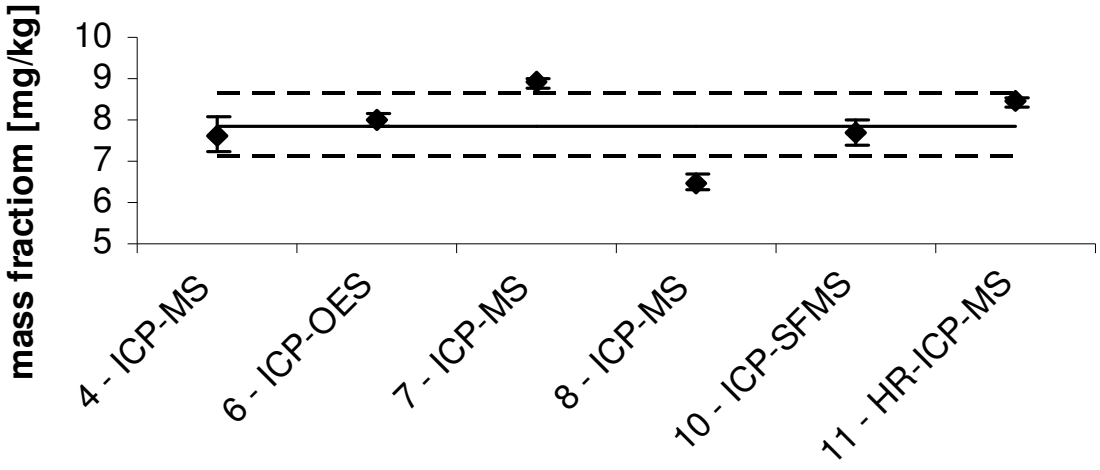

Figure A31: Results for the aqua regia extractable content of Co as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab 7 (ICP-MS) = 1.8 mg/kg, Lab 8 (ICP-MS) = 5%, respectively

Table A28: Individual results as reported for the aqua regia extractable content of Cr (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - ICP-OES	36.2	35.3	34.2	36.2	34.6	34.3	35.1	0.9
4 - ICP-MS	30.0	29.4	31.8	32.5	32.1	30.5	31.0	1.3
6 - ICP-OES	30	32	30	29	30	31	30	1
7 - ICP-MS	32.7	28.3	32.5	33.0	32.0	32.5	31.8	1.8
9 - ICP-MS	22.7	23	22.8	23.3	23.4	22.9	23.0	0.3
10 - ICP-SFMS	32	29	31	31	31	30	31	1
11 - ICP-OES	30.7	34.2	34.1	31.0	32.3	32.2	32.4	1.5

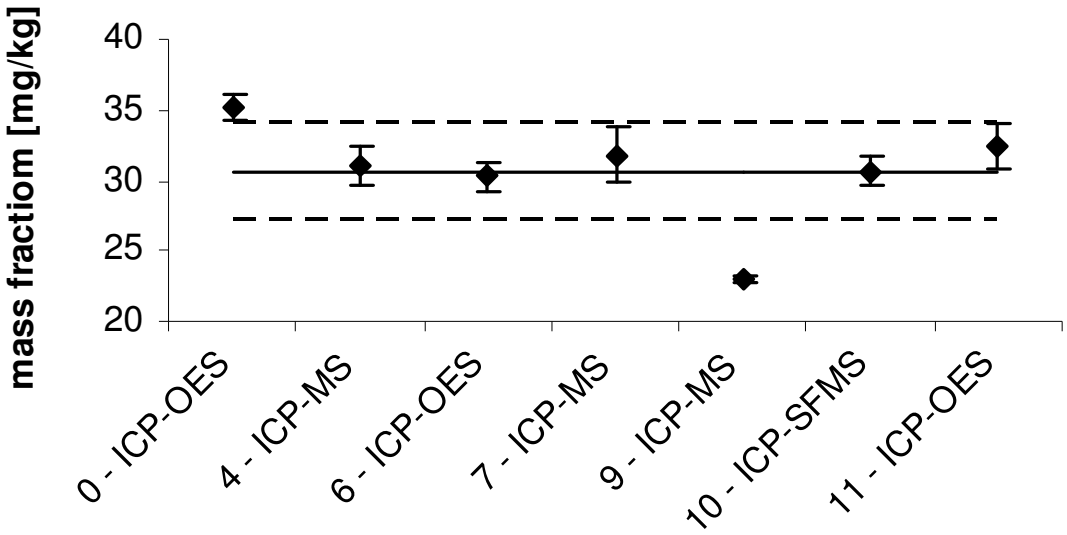

Figure A32: Results for the aqua regia extractable content of Cr as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab9 (ICP-MS) = 20 %

Table A29: Individual results as reported for the aqua regia extractable content of Cu (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - ICP-OES	14.2	13. 8	13.2	13.8	13.5	13.2	13.6	0.4
4 - ICP-MS	12.3	12.7	12.6	12.1	11.7	12.4	12.3	0.4
6 - ICP-OES	12.4	12.8	12.7	12.2	12.5	12.8	12.6	0.2
7 - ICP-MS	11.2	13.1	12.9	13.2	12.6	13.4	12.7	0.8
8 - ICP-OES	13.0	13.5	13.2	13.2	13.4	13.1	13.2	0.2
9 - ICP-MS	10.2	10.2	10.0	10.7	10.2	10.1	10.2	0.2
10 - ICP-SFMS	12.5	12.2	12.1	13.4	13.6	12.4	12.7	0.6
11 - ICP-OES	11.8	12.0	12.2	12.1	12.3	12.1	12.1	0.2
12 - ICP-OES	12.3	11.9	11.8	11.5	12.4	12.5	12.1	0.4

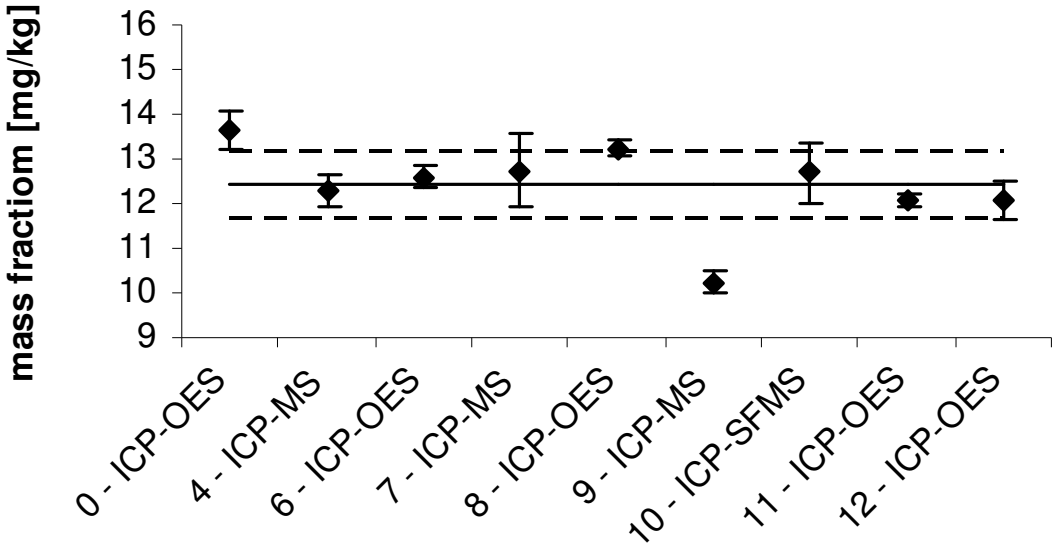

Figure A33: Results for the aqua regia extractable content of Cu as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab9 (ICP-MS) = 20 %

Table A30: Individual results as reported for the aqua regia extractable content of Mn (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - ICP-OES	408	392	395	407	404	399	401	7
4 - ICP-MS	389.2	376.3	409.3	373.3	408.3	400.7	392.9	15.8
6 - ICP-OES	380.0	403.9	390.5	381.6	383.4	400	389.9	10.1
7 - ICP-OES	415	422	415	419	421	418	418	3
8 - ICP-MS	374	374	385	380	373	373	377	5
10 - ICP-SFMS	405	365	374	400	369	382	382	17
11 - ICP-OES	367.8	366.9	377.0	361.5	369.6	369.8	368.8	5.1
12 - ICP-OES	374	366	364	361	373	374	369	6

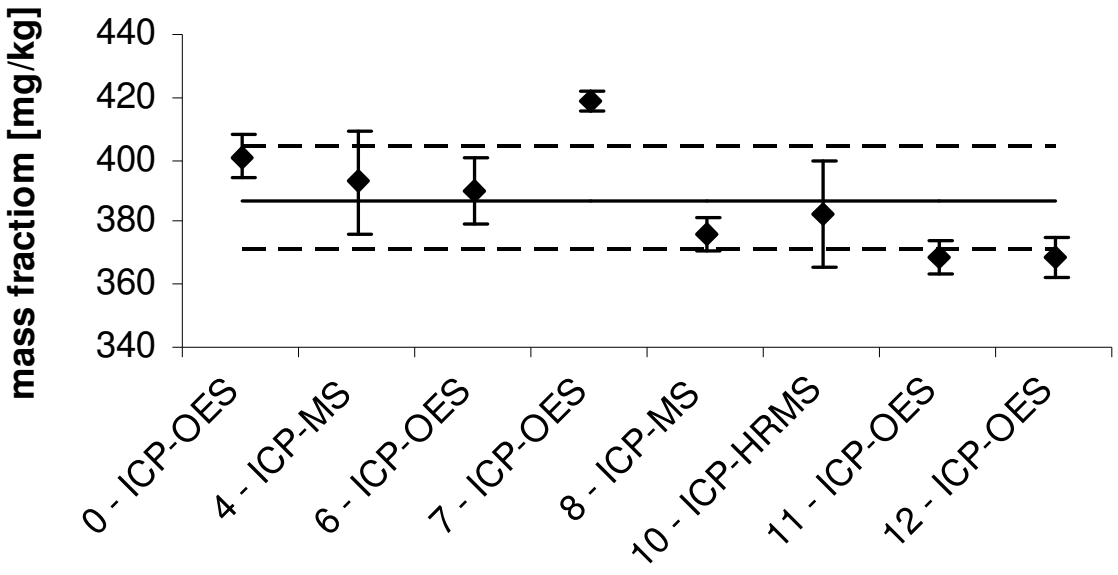

Figure A34: Results for the aqua regia extractable content of Mn as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab7 (ICP-OES) = 83.4 mg/kg

Table A31: Individual results as reported for the aqua regia extractable content of Ni (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - ICP-OES	26	25	26	26	27	26	26	1
4 - ICP-MS	20.6	20.0	21.4	18.4	20.7	21.0	20.3	1.1
6 - ICP-OES	20	22	21	20	20	22	21	1
7 - ICP-MS	19.9	23.0	22.6	22.3	23.4	22.7	22.3	1.2
8 - HR-ICP-MS	20.7	20.3	20.7	20.1	20.0	20.3	20.4	0.3
9 - ICP-MS	20.0	20.2	19.8	20.5	20.2	19.8	20.1	0.3
10 - ICP-SFMS	24.6	21.9	23.3	24.3	23.0	22.1	23.2	1.1
11 - ICP-OES	22.0	22.7	23.2	21.5	22.6	22.7	22.5	0.6
12 - ICP-OES	21.9	21.5	22.1	21.3	22.2	22	21.8	0.4

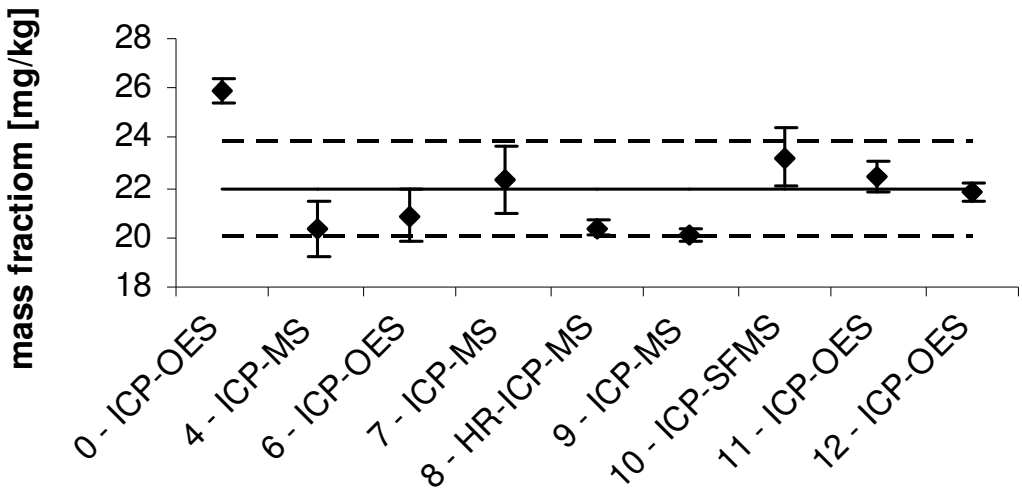

Figure A35: Results for the aqua regia extractable content of Ni as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab0 (ICP-OES) = 3.9 mg/kg

Table A32: Individual results as reported for the aqua regia extractable content of Pb (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
4 - ICP-MS	32.2	31.6	32.1	31.5	32.5	31.8	32.0	0.4
6 - ICP-OES	31.4	29.6	30.3	30.4	30.6	30.9	30.5	0.6
7 - ICP-MS	33.5	32.8	33.6	32.8	32.7	33.5	33.2	0.4
8 - ICP-MS	33.3	32.3	33.8	32.3	32.6	31.9	32.7	0.7
9 - ICP-MS	32.5	32.5	31.1	31.6	31.8	31.0	31.7	0.6
10 - ICP-SFMS	34.1	32.4	35.0	34.2	34.9	32.2	33.8	1.2
11 - HR-ICP-MS	31.3	31.5	31.1	30.2	31.7	32.8	31.5	0.9

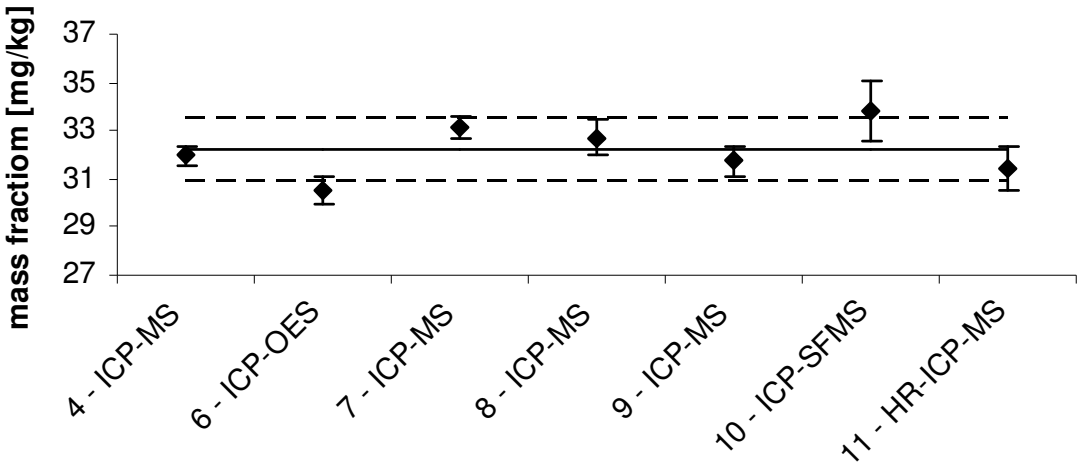

Figure A36: Results for the aqua regia extractable content of Pb as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Table A33: Individual results as reported for the aqua regia extractable content of Zn (SD= standard deviation)

Labcode	Results of the replicate measurements [mg/kg]						Mean [mg/kg]	SD [mg/kg]
0 - ICP-OES	50.8	48.5	48.8	49.7	49.9	48.7	49.4	0.9
4 - ICP-MS	51	49	49	45	47	47	48	2
6 - ICP-OES	47.7	50.7	48.5	46.3	47	48.9	48.2	1.6
7 - ICP-OES	53.0	53.4	52.7	52.3	53.5	53.0	53.0	0.4
8 - ICP-MS	48.2	46.8	47.1	46.9	46.6	47.2	47.1	0.6
9 - ICP-MS	49.0	50.0	52.0	48.7	48.8	51.4	49.8	1.5
10 - ICP-SFMS	54.3	52.7	52.4	54.1	50.6	53.7	53.0	1.4
12 - ICP-OES	51.1	50.3	50.9	50.4	51.0	51.2	50.8	0.4

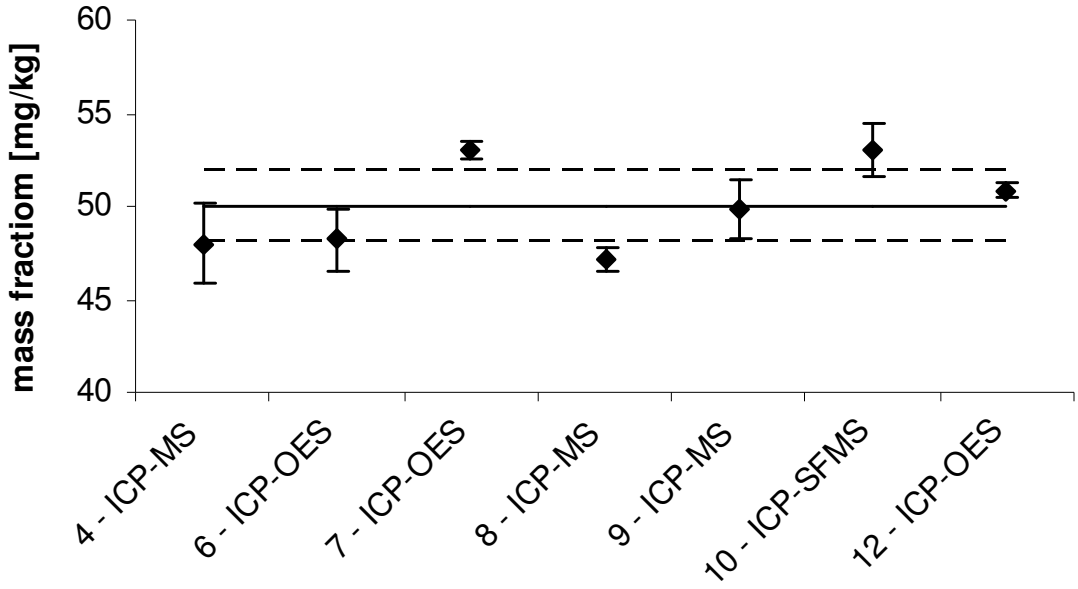

Figure A37: Results for the aqua regia extractable content of Zn as used in the characterisation. Uncertainty bars represent the 95 % confidence interval of each lab's results. (__: certified value, ----: expanded uncertainty of the certified value)

Note: Lab7 (ICP-OES) = 10.6 mg/kg, Lab 8 (ICP-MS) = 2.4 mg/kg

Annex 6: Data for the quality control sample (BCR-141R)

Table A34: Individual results as reported for the total content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in the quality control sample (BCR-141R). Data deviating 15 % or more from the certified value (20 % for As) is indicated by a grey background.

Lab code	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
1	8	14	14	182	46	702	99	73	253
2	65.4	13.2	8.3	164	164.3	605	72.8	49.2	224
3	-	12.3	-	174	41.4	-	85.3	49.5	238
4	9.7	12.5	10.2	187	37.5	686	96.9	51.9	228
5	8.1	7.4	10.5	243	45.6	615	105.8	40.0	234
6	7.5	-	25.8	216	53.4	684	102.0	57.6	272
7	6.0	12.8	10.4	195	48.6	680	101.4	53.6	272
8	7.7	24.2	9.7	157	45.5	632	85.4	80.7	259
9	9.9	15.3	10.1	180	48.0	696	100	58.1	301
10	16.2	13.7	9.9	191	45.8	614	99.3	56.8	258
11	-	-	8.0	180	44.9	689	97.8	39.4	284
Certified value		14.6 ± 0.5	10.5 ± 0.4	195 ± 7	46.4 ± 1.8	683 ± 16	102.9 ± 2.3	57.2 ± 1.2	283 ± 5
Indicative value	8.8 ± 0.5								

Table A35: Individual results as reported for the aqua regia extractable content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in the quality control sample (BCR-141R). Data deviating 15 % or more from the certified value (20 % for As) is indicated by a grey background.

Lab code	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
0	-	-	-	130	48.4	629	88	63.3	237
1	5	12	8	135	31	547	76	41	241
2	30.5	13.1	5.7	118	37.5	571	70	47.5	218
4	6.5	12.4	9.1	133	43	627	86	47.8	245
5	7.8	6.9	6	80	26.6	415	59	29.6	153
6	6.8	14.0	8.5	127	48.4	618	87	47.8	259
7	8.2	13.1	9.6	127	45.4	630	85	46	238
8	6.0	13.1	8.3	108	45.6	634	84	49.8	262
9	7.9	13.6	7.4	118	40.7	506	98	51.8	259
10	6.4	14.2	9.4	135	44.4	655	94	50.8	274
11	11.9	13.1	9.0	135	42.0	580	95	47.7	213
12	9.7	13	7.4	109	41.9	560	80.0	42.7	250
Certified value		14.0 ± 0.4	9.2 ± 0.5	138 ± 5	46.9 ± 1.8	653 ± 16	94 ± 5	51.3 ± 2.0	270 ± 8

European Commission

EUR 24486 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: The Certification of the Mass Fraction of the Total Content and the Aqua Regia Extractable Content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in Loam Soil, Certified Reference Material ERM®-CC141
Author(s): A. Birgersson-Liebich, T. Venelinov, A. Santoro, A. Held
Luxembourg: Publications Office of the European Union
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Abstract
This report describes the preparation and certification of a loam soil Certified Reference Material (CRM) ERM-CC141. The CRM was processed and certified by the European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

The CRM was prepared from a loamy soil with a natural level of metals. After being dried and milled, the resulting soil powder was put into amber glass bottles containing a minimum of 24 g of sample.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

The CRM has been certified for its total and its aqua regia extractable (according to ISO 11466) content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn.

The main purpose of the material is to assess method performance and check analytical results. As any reference material, it can also be used for control charts or validation studies.

Total content	Mass fraction based on dry mass	
	Certified value [1] [mg/kg]	Uncertainty [2] [mg/kg]
As	9.9	1.5
Cd	0.35	0.05
Co	8.5	0.5
Cr	86	8
Cu	14.4	1.4
Mn	464	18
Ni	26.4	2.4
Pb	41	4
Zn	57	4
Aqua regia extractable content according to ISO 11466	Mass fraction based on dry mass	
	Certified value [1] [mg/kg]	Uncertainty [2] [mg/kg]
As	7.5	1.4
Cd	0.25	0.04
Co	7.9	0.9
Cr	31	4
Cu	12.4	0.9
Mn	387	17
Ni	21.9	1.6
Pb	32.2	1.4
Zn	50	4

1) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values are traceable to the SI.

2) Expanded uncertainty with a coverage factor $k = 2$ according to the Guide for the Expression of Uncertainty in Measurement, corresponding to a level of confidence of about 95 %.

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